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Full Theoretical Cycle for both Ethene and Propene Formation during Methanol-to-Olefin Conversion in H-ZSM-5

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The methanol-to-olefin (MTO) process, catalyzed by acidic zeolites such as H-ZSM-5, provides an increasingly important alternative to the production of light olefins from crude oil. However, the various mechanistic proposals for methanol-to-olefin conversion have been strongly disputed for the past several decades. This work provides theoretical evidence that the experimentally suggested 'alkene cycle', part of a co-catalytic hydrocarbon pool, offers a viable path to the production of both propene and ethene, in stark contrast to the often-proposed direct mechanisms. This specific proposal hinges on repeated methylation reactions of alkenes, starting from propene, which occur easily within the zeolite environment. Subsequent cracking steps regenerate the original propene molecule, while also forming new propene and ethene molecules as primary products. Because the host framework stabilizes intermediate carbenium ions, isomerization and deprotonation reactions are extremely fast. Combined with earlier joint experimental and theoretical work on polymethylbenzenes as active hydrocarbon pool species, it is clear that, in zeolite H-ZSM-5, multiple parallel and interlinked routes operate on a competitive basis.

Introduction

To meet the ever increasing demand for oil-based chemicals despite waning oil reserves, the development of new technologies from alternative feedstock is a general concern for both scientific and industrial communities. One of the most prominent emerging technologies is the methanol-to-olefin (MTO) process, catalyzed by acidic zeolites, such as H-ZSM-5, or by nanoporous zeotype materials, such as H-SAPO-34.[1] Herein, we report on a complete route from a theoretical viewpoint of the recently proposed 'alkene route,'[2] in which alkenes act as essential co-catalysts in addition to the zeolite framework. This hypothesis provides a complete, viable low-energy pathway to both ethene and propene production in H-ZSM-5.

Despite considerable effort from experimental and theoretical research, the reaction mechanism of the MTO process has proven to be extremely difficult to unravel, ever since its discovery in the 1970s.[1] Recent interest in the mechanism was fueled by a surge in oil prices; MTO conversion allows the petrochemical industry to bypass crude oil as a fundamental feedstock. Methanol can be made from synthesis gas, which in turn can be formed from almost any gasifiable carbonaceous species, such as natural gas, coal, biomass and organic waste. The MTO process converts methanol into light olefins, such as ethene and propene, which serve as basic building blocks for the entire petrochemical industry and polymerization processes in particular. As a result, ethene and propene are increasingly in demand.

Historically, almost all attention focused on 'direct mechanisms', for which C–C coupling occurs from C_1 species, such as methanol and dimethyl ether, only. In the last decade, however, intensive experimental[3,4] and theoretical[5–7] research has shown that the direct routes do not explain the initial C–C coupling, opening the door to new mechanistic proposals. The most recent experimental developments strongly support an alternative 'hydrocarbon pool' mechanism,[8] in which organic reaction centers in the zeolite pores act as olefin-producing co-catalysts. The basic ideas were originally proposed in the 1980s and 1990s by Dessau, Dahl, and Kolboe,[9,10] but have since remained largely ignored by the scientific community. The failure of the direct routes and additional experimental proof for the hydrocarbon pool mechanism has reignited interest in the proposed hydrocarbon pool mechanism.[11–13]

In a recent joint experimental/theoretical effort, we managed to construct a complete working catalytic cycle based on methylbenzenes as crucial hydrocarbon pool species in H-ZSM-5 following the 'paring' route' and producing isobutene.[14] The experimentally observed energy barriers were significantly lower than those calculated for the direct routes.[6] However, this type of cycle has so far failed to theoretically explain the ethene production witnessed in H-ZSM-5, as energy barriers for ethene elimination in the 'side-chain' route were found to be too high.[15] To our knowledge, no full cycle producing

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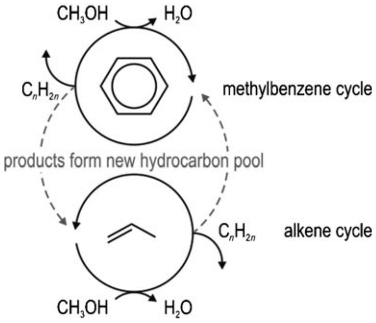
ethene has been theoretically validated, though fragmented reaction steps have been documented before.

Polymethylbenzenes might not be the only active hydrocarbon pool species toward olefin formation, even though they have long been commonly regarded as the most important hydrocarbon pool species. While this probably still holds for zeolites with the BEA or CHA topology, recent experiments have shown that the archetypical MTO catalyst H-ZSM-5 (with more limited space in the MFI-topology) could form an important exception. Svelle et al. demonstrated that the higher methylbenzenes, normally the most active species, are virtually unreactive in the pores of H-ZSM-5.[16] Molecular simulations show that this is mainly due to transition state shape selectivity; the narrow channels and restricted space at channel intersections limit the reactivity of bulky methylbenzenes.[17] The original proposal by Dessau, based on successive methylation and cracking reactions of C_{3+} alkenes, was revived through ^{13}C labeling experiments,[9] providing a parallel route for the production of light olefins on zeolite H-ZSM-5. In more detailed research by Svelle et al., ethene appeared to be formed solely from the lower methylbenzenes (on the basis of equal ^{13}C incorporation in ethene and lower methylbenzenes), whereas propene and higher alkenes would be formed from alkene methylation and interconversion.[18]

These observations led to the proposal of a complete dual cycle mechanism, in which a polymethylbenzene cycle would yield predominantly ethene, and an alkene cycle would mainly yield propene and higher alkenes (Scheme 1). These cycles are interconnected since the polymethylbenzene cycle also produces propene as a product (which can act directly as a co-catalyst in the alkene cycle),[14] and conversely propene molecules can oligomerize to form a new polymethylbenzene catalyst, as has been shown from theoretical viewpoint.[19]

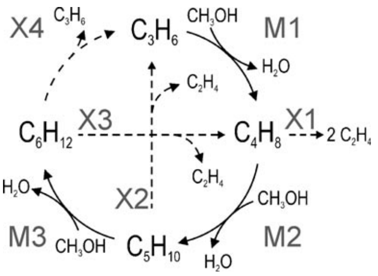


Scheme 1. Two possible hydrocarbon pool cycles, based on a methylbenzene and alkene organic co-catalyst present in the zeolite pores. Both cycles convert methanol into light olefins and water, but with different ethene/propene selectivities. The two cycles do not operate independently, but are interconnected since the products can either act as new co-catalysts directly (for the alkene cycle) or undergo oligomerization and cyclization to form new aromatic co-catalysts (used in the methylbenzene cycle).

Such a dual cycle might eventually allow full control of the propene-to-ethene ratio, for which a thorough understanding and comparison of all elementary steps is of the utmost importance. In this study, the elementary reactions of the C_{3+} alkene cycle are modeled using quantum chemical techniques to identify a complete pathway with low energy barriers (for more information on the level of theory, see the Methods section and Refs. [20] and [21]). To verify whether olefin formation proceeds along this route and whether propene formation is indeed preferred to ethene formation, the previously suggested cycle[16] is extended so that no a priori assumptions are made regarding the nature of the products formed. However, some limitations have been made towards branching intermediates to prevent an excessively complicated scheme. The main questions to be answered from a theoretical perspective are the following: Can the alkene proposal be considered a viable olefin-producing route? How does it relate to the direct mechanisms and to the methylbenzene route? How might it influence the ethene/propene product selectivity?

Results and Discussion

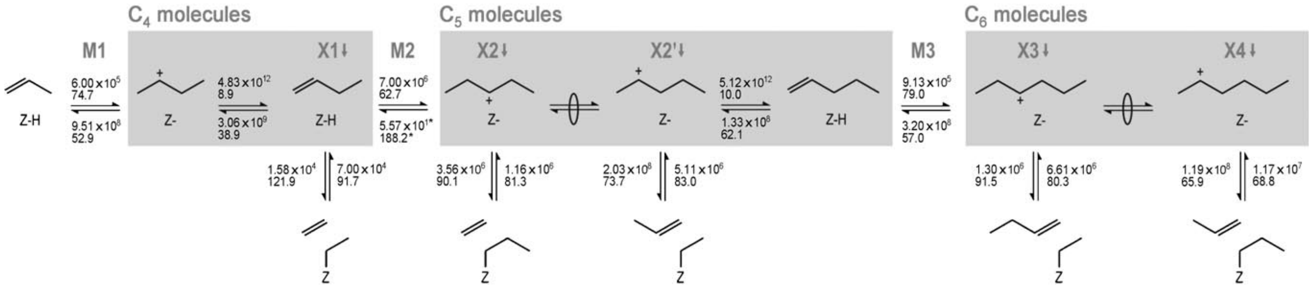
A simplified picture of the studied cycle is shown in Scheme 2. Starting with a single propene molecule, chain growth proceeds through successive methylation steps by methanol (M1–M3), finally forming hexene. For clarity, only methylation of 1-alkenes, through which no branching of the carbon skeleton occurs, is considered in this study. Accordingly, isomerization reactions that ensure a proper placement of the double bond need to be taken into account before each methylation. Ultimately, the cracking of these longer alkenes (reactions X1–X4) results in the production of light olefins, notably ethene and propene.



Scheme 2. Full catalytic cycle near an acid site in zeolite ZSM-5, starting from propene (top). Several methylation steps by methanol (M1–M3) provide chain growth, whereas cracking steps (X1–X3) form new ethene and propene products and replenish the original hydrocarbon pool.

We chose to limit the calculations to linear alkenes to prevent excessive cluttering of the reaction diagrams. This choice was based on the fact that branched molecules will crack more easily than linear molecules,[22] which makes the reaction barriers considered in this study representative of the upper limit of such reactions. If a full cycle for linear alkenes proves to be fully operational, branched alkenes will only speed up the process. For a detailed theoretical study on the methylation to *trans*-2-butene, we refer to earlier work.[21]

Most of the reactions under study herein have already been studied theoretically,[19,23–26] albeit on varying levels of theory and using a wide scale of theoretical methods, ranging from



Scheme 3. Overview of the full alkene cycle forming both alkenes and alkoxides: methylation steps (M1–M3, shown horizontally) and cracking steps (X1–X4, shown vertically) correspond to those in Scheme 2. Numbers refer to reaction rates at 673 K (in s^{-1}, top value) and reaction barriers (in $kJ\,mol^{-1}$, bottom value).

small cluster calculations to full periodic calculations, rendering direct comparison almost impossible. Even though isolated steps might be feasible, it remains unclear whether a complete route is a solid alternative to the direct mechanisms. Therefore, our goal in this work is to treat all reactions uniformly, including the effect of the surrounding zeolite framework, and fill in the missing gaps. This approach allows full comparison between the various reaction types, as well as with previous work on the methylbenzene hydrocarbon pool.

Scheme 3 gives a more detailed overview of the full cycle, expanded from Scheme 2. Full details on how reaction rates and barriers were calculated can be found in the Methods section and in previous work.[21]

Methylation

The reaction barriers for methylation of alkenes (60–80 $kJ\,mol^{-1}$) are lower than those previously reported for methylation of higher polymethylbenzenes (±150 $kJ\,mol^{-1}$) in H-ZSM-5 (horizontal arrows in Scheme 3, reactions M1–M3).[14,17] The latter values were obtained without dispersion interactions, but these corrections typically lie in the range of 20–30 $kJ\,mol^{-1}$ for methylation reactions, thus making them still larger than the here obtained values.[15,17,23] The reaction barriers in the MFI topology depend largely on the number of methyl substituents, as reported previously.[17] The here-obtained values fall in exactly the same range as those for the methylation of -hexamethylbenzene in the CHA topology of H-SSZ-13 (the aluminosilicate analogue of SAPO-34) or the lower methylbenzenes in H-ZSM-5 (also in the range of 60–80 $kJ\,mol^{-1}$).[17] As far as methylation is concerned, the small alkenes seem to be very similar in reactivity compared to the active methylbenzenes, and much higher in reactivity compared to relatively inactive higher methylbenzenes when space constraints are imposed. These results demonstrate that methylation of alkenes and methylbenzenes will be competitive and dependent on the available species within the zeolite pores.

The resulting product species is a secondary carbenium ion (Scheme 3), which is easily deprotonated to form the subsequent alkene; barriers are no higher than 10 $kJ\,mol^{-1}$. These low barriers for deprotonation were already obtained without any assistance of the residual water molecule. There is one notable exception: the intrinsic reaction coordinate (IRC) calculation reveals that, after methylation of butene, the residual water molecule attaches to the carbenium ion, forming an oxonium ion instead (Scheme 3, asterisk for the reverse reaction M2). This structure is shown in Figure 1. The observed additional stabilizing effect will be further investigated in future work, as it suggests that the abundance of water molecules within the zeolite cages will assist in stabilizing crucial carbenium ion intermediates. The deprotonation steps have not been explicitly labeled in Scheme 2, and are shown within the grey boxes in Scheme 3 (energy barriers of 8.9 and 10.0 $kJ\,mol^{-1}$).

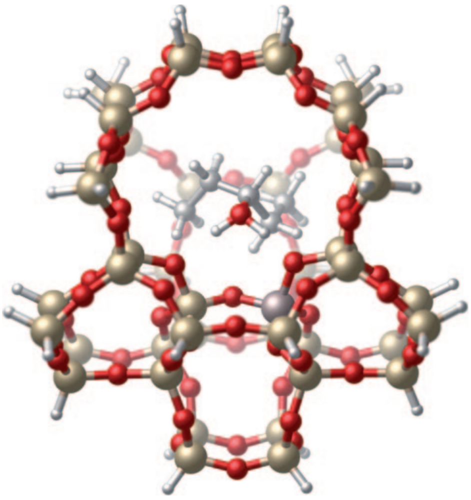


Figure 1. The product for the second methylation reaction (M2) within the ZSM-5 framework. The oxygen atom from the water molecule coordinates with the positively charged carbon atom, further stabilizing this species.

Isomerization

Isomerization can occur both in a one-step and a two-step (through an intermediate alkoxide)[28] procedure starting from neutral molecules. However, to date, isomerization studies have always been considered from neutral species. Using the products obtained from the preceding steps, we know that secondary carbenium ions are formed after the methylation step. These ions can undergo intramolecular hydride shifts which are virtually barrierless (10–15 $kJ\,mol^{-1}$) even outside the zeolite environment and lead to an equilibrium between different secondary carbenium ions of the same chain length, which is completely in line with experimental observations.[29] Because the carbon number does not change, these hydride shift reactions can be found as barrierless reactions alongside the deprotonation reactions (Scheme 3, grey boxes). Combined with the equally fast deprotonation steps (barriers around 10 kJ mol^{-1}), the double bond can be reasonably assumed to be in any desired position, fully allowing the construction of the simplified complete cycle consisting solely of linear alkenes in this study. Of course, it is important to restate that branched alkenes will be formed as well and actually will be preferential methylation products. Furthermore, they are believed to crack more easily as stated earlier, and will, therefore, have even lower energy barriers.

Cracking

Once the chain reaches the desired length, ethene and propene can be formed through cracking reactions (Scheme 3, reactions X1–X4), even for linear alkenes. β-Scission on a secondary carbenium ion was the main cracking reaction modeled in this study but, alternatively, cracking can also occur through a protonated cyclopropyl species (PCP). Cracking of alkenes with five or more carbon atoms seems to occur readily (barriers of 70–90 kJ mol^{-1}), with the β-scission mechanism being generally favored over the PCP-type mechanism. The cracking products appear both as alkenes and as framework-bound alkoxides, requiring an additional desorption step; the latter step has already been elaborately documented.[19,28]

Our theoretical results reveal that cracking of longer alkenes to form propene (Schemes 2 and 3; X2, X2′, and X4,) is generally faster than that to form ethene (X1 and X3), confirming the experimentally observed predominant propene selectivity of this route, yet not completely excluding residual ethene formation along this route either. This is in total agreement with previous experimental work on alkene cracking within acidic zeolites[29] and also with the observation that the alkene route would be propene heavy in comparison to other hydrocarbon pool cycles.[16,18,30] Taking into account the possibility of alkene formation from polymethylbenzenes, we observe a delicate balance for product selectivity based on the size and shape of the nanometer-sized pores. Since none of the considered steps has excessively high energy barriers, we can also conclude that the propene route is a viable olefin-producing route from theoretical viewpoint as well, confirming the recent experimental statements.[16]

Conclusions

In summary, our theoretical calculations have shown that the alkene cycle offers a viable path to the production of both major olefin products. Methylation occurs equally as fast as that of the most active methylbenzenes, but is not subject to any steric hindrance. Several cracking steps are possible depending on chain length, resulting in the production of not only propene but also ethene, yet still with a slight preference for the former. Isomerization and deprotonation reactions are extremely fast, which will result in a wide variety of linear and branched alkenes formed. Going beyond our earlier theoretical work on the polymethylbenzenes as active hydrocarbon pool molecules, we can conclude that, in H-ZSM-5, multiple parallel and interlinked routes operate on a competitive basis. Although these routes are based on totally different hydrocarbon pool co-catalysts, the most active routes show similar energy barriers for the rate determining steps.

With respect to our choice to only consider linear alkenes, we can firmly conclude that the alkene route is definitely an active olefin-producing route. Since cracking steps occur faster for branched alkenes, any similar route containing branched alkenes along the way is likely to have even lower energy barriers. We also note that the energy barrier for cracking of linear alkenes becomes competitive with the energy barrier for methylation once we reach a linear C_6 molecule. This might indicate that the most effective route for linear alkenes would consist of 3 subsequent methylation steps, after which the molecule cracks into two propene species. Reaction rates can not easily be compared between these two reaction families, since they will be dependent on the methanol and water concentrations in the pores. Nevertheless, comparison with experimental data shows that the calculated energy barriers are highly accurate with this level of theory.[21]

Additional insights into these parallel cycles, and into the role of the zeolite framework on their relative productivity, might lead to the highly coveted control over the ethene/propene ratio. Additionally, favoring the alkene route over the methylbenzene route could also provide a means to prevent coke formation and delay ultimate deactivation of the catalyst,[17,19] since this route is less likely to form diffusion-limiting polyaromatics.

Theoretical methods

All geometries were optimized at the ONIOM(B3LYP/6-31g(d):MNDO) level of theory on a large 8T:46T H-ZSM-5 cluster with the Gaussian03 software.[31] Saturating hydrogen atoms were held fixed to mimic crystallographic behavior. Subsequently single-point calculations at the ONIOM(B3LYP/6-31g(d):HF/6-31g(d)) level of theory were performed. These energies were further refined by including van der Waals corrections at the B3LYP-D level of theory with the Orca software package.[32] A similar level of theory was used for the paring route and side-chain route in the polymethylbenzene cycle. The paring route still lacked dispersion corrections, but both for the side-chain route and the alkene route, we found dispersion corrections to be mainly significant for adsorption energies, but less so for reaction barriers (typical changes of up to 10 kJ mol^{-1}). Kinetic coefficients were obtained using classical TST and the PHVA methods[33] as used in previous work.[14] Only with the surrounding zeolite environment did secondary carbenium ions occur as minima, albeit in a shallow potential well. For visualization and kinetic analysis, we used in-house developed software programs,[34,35] as well as CYLview.[36]

The computational method employed herein, which was also used in previous work,[14,15] has recently been the subject of an extensive theoretical benchmarking study,[21] going beyond the original level-of-theory study for ONIOM calculations in zeolites in 2005.[20] More specifically, for the methylation reactions studied in this paper (M1–M2), the obtained results are very close to extremely high-level periodic results and experimental observations,[24] especially when the DFT-D corrections are included. Compared to the landmark benchmarking study by Sauer and co-workers,[24] this method has the additional advantage that it is computationally very efficient and allows for a wide range of reactions to be studied within a realistic computational time frame. In a recent study on related reactions, a variety of other theoretical procedures and functionals were also tested.[37]

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[1] M. Stöcker, *Microporous Mesoporous Mater.* **1999**, *29*, 3 – 48.
[2] M. Bjorgen, S. Svelle, F. Joensen, J. Nerlov, S. Kolboe, F. Bonino, L. Palumbo, S. Bordiga, U. Olsbye, *J. Catal.* **2007**, *249*, 195 – 207.
[3] W. G. Song, D. M. Marcus, H. Fu, J. O. Ehresmann, J. F. Haw, *J. Am. Chem. Soc.* **2002**, *124*, 3844 – 3845.
[4] D. M. Marcus, K. A. McLachlan, M. A. Wildman, J. O. Ehresmann, P. W. Kletnieks, J. F. Haw, *Angew. Chem.* **2006**, *118*, 3205 – 3208; *Angew. Chem. Int. Ed.* **2006**, *45*, 3133 – 3136.
[5] D. Lesthaeghe, V. Van Speybroeck, G. B. Marin, M. Waroquier, *Ind. Eng. Chem. Res.* **2007**, *46*, 8832 – 8838.
[6] D. Lesthaeghe, V. Van Speybroeck, G. B. Marin, M. Waroquier, *Angew. Chem.* **2006**, *118*, 1746 – 1751; *Angew. Chem. Int. Ed.* **2006**, *45*, 1714 – 1719.
[7] D. Lesthaeghe, V. Van Speybroeck, G. B. Marin, M. Waroquier, *Chem. Phys. Lett.* **2006**, *417*, 309 – 315.
[8] J. F. Haw, D. M. Marcus, *Top. Catal.* **2005**, *34*, 41 – 48.
[9] R. M. Dessau, *J. Catal.* **1986**, *99*, 111 – 116.
[10] I. M. Dahl, S. Kolboe, *J. Catal.* **1994**, *149*, 458 – 464.
[11] W. G. Song, J. F. Haw, J. B. Nicholas, C. S. Heneghan, *J. Am. Chem. Soc.* **2000**, *122*, 10726 – 10727.
[12] J. F. Haw, W. G. Song, D. M. Marcus, J. B. Nicholas, *Acc. Chem. Res.* **2003**, *36*, 317 – 326.
[13] U. Olsbye, M. Bjorgen, S. Svelle, K. P. Lillerud, S. Kolboe, *Catal. Today* **2005**, *106*, 108 – 111.
[14] D. M. McCann, D. Lesthaeghe, P. W. Kletnieks, D. R. Guenther, M. J. Hayman, V. Van Speybroeck, M. Waroquier, J. F. Haw, *Angew. Chem.* **2008**, *120*, 5257 – 5260; *Angew. Chem. Int. Ed.* **2008**, *47*, 5179 – 5182.
[15] D. Lesthaeghe, A. Horré, M. Waroquier, G. B. Marin, V. Van Speybroeck, *Chem. Eur. J.* **2009**, *15*, 10803 – 10808.
[16] S. Svelle, F. Joensen, J. Nerlov, U. Olsbye, K. P. Lillerud, S. Kolboe, M. Bjorgen, *J. Am. Chem. Soc.* **2006**, *128*, 14770 – 14771.
[17] D. Lesthaeghe, B. De Sterck, V. Van Speybroeck, G. B. Marin, M. Waroquier, *Angew. Chem.* **2007**, *119*, 1333 – 1336; *Angew. Chem. Int. Ed.* **2007**, *46*, 1311 – 1314.
[18] S. Svelle, U. Olsbye, F. Joensen, M. Bjorgen, *J. Phys. Chem. C* **2007**, *111*, 17981 – 17984.
[19] M. Vandichel, D. Lesthaeghe, J. Van der Mynsbrugge, M. Waroquier, V. Van Speybroeck, *J. Catal.* **2010**, *271*, 67 – 78.
[20] X. Solans-Monfort, M. Sodupe, V. Branchadell, J. Sauer, R. Orlando, P. Ugliengo, *J. Phys. Chem. B* **2005**, *109*, 3539 – 3545.
[21] V. Van Speybroeck, J. Van der Mynsbrugge, M. Vandichel, K. Hemelsoet, D. Lesthaeghe, A. Ghysels, G. B. Marin, M. Waroquier, unpublished results.
[22] T. Wakayama, H. Matsuhashi, *J. Mol. Catal. A: Chem.* **2005**, *239*, 32 – 40.
[23] S. Svelle, B. Arstad, S. Kolboe, O. Swang, *J. Phys. Chem. B* **2003**, *107*, 9281 – 9289.
[24] S. Svelle, C. Tuma, X. Rozanska, T. Kerber, J. Sauer, *J. Am. Chem. Soc.* **2009**, *131*, 816 – 825.
[25] Y.-X. Sun, J. Yang, L.-F. Zhao, J.-X. Dai, H. Sun, *J. Phys. Chem. C* **2010**, *114*, 5975 – 5984.
[26] S. Svelle, S. Kolboe, O. Swang, U. Olsbye, *J. Phys. Chem. B* **2005**, *109*, 12874 – 12878.
[27] K. Hemelsoet, A. Nollet, M. Vandichel, D. Lesthaeghe, V. Van Speybroeck, M. Waroquier, *ChemCatChem* **2009**, *1*, 373 – 378.
[28] A. Bhan, Y. V. Joshi, W. N. Delgass, K. T. Thomson, *J. Phys. Chem. B* **2003**, *107*, 10476 – 10487.
[29] Y. V. Kissin, *Catal. Rev. Sci. Eng.* **2001**, *43*, 85 – 146.
[30] M. Bjørgen, F. Joensen, K. P. Lillerud, U. Olsbye, S. Svelle, *Catal. Today* **2009**, *142*, 90 – 97.
[31] *Gaussian 03*, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, 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, A. 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**.
[32] *Orca version 2.7.0*, F.Neese, University of Bonn, Germany, **2008**.
[33] A. Ghysels, D. Van Neck, V. Van Speybroeck, T. Verstraelen, M. Waroquier, *J. Chem. Phys.* **2007**, *126*, 224102.
[34] A. Ghysels, T. Verstraelen, K. Hemelsoet, V. Van Speybroeck, M. Waroquier, *J. Chem. Inf. Model.* **2010**, *50*, 1736 – 1750.
[35] T. Verstraelen, V. Van Speybroeck, M. Waroquier, *J. Chem. Inf. Model.* **2008**, *48*, 1530 – 1541.
[36] CYLview BETA 1.0, Copyright **2006–2008** Claude Y. Legault.
[37] B. Chan, L. Radom, *Can. J. Chem.* **2010**, *88*, 866 – 876.

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