From Zeolites to Porous MOF Materials – the 40th Anniversary
of International Zeolite Conference
R. Xu, Z. Gao, J. Chen and W. Yan (Editors)

Refinement of the supramolecular concept in methanol-to-olefin catalysis

D. Lesthaeghe[a], V. Van Speybroeck[a], G. B. Marin[b] and M. Waroquier[a]

[a] Center for Molecular Modeling, Ghent University, Proeftuinstraat 86, B-9000 Gent, Belgium

[b] Laboratorium voor Petrochemische Techniek, Ghent University, Krijgslaan 281-S5, B-9000 Gent, Belgium

ABSTRACT

The supramolecular character of methanol-to-olefin conversion in acidic zeolites is thoroughly investigated from a theoretical viewpoint. State-of-the-art modeling techniques have not only led to an absolute rejection of the intensively studied direct mechanisms, but have also provided additional insights into the alternative hydrocarbon pool proposal. The role of various external factors such as zeolite topology on the formation of crucial carbenium ions is discussed and the establaished supramolecular picture is refined.

1. INTRODUCTION

Light olefins are vital components in the petrochemical industry and are traditionally obtained by steam cracking of crude oil fractions. However, because the finite oil reserves will not be able to meet the ever-increasing demand for oil-based chemicals, new developments currently focus on technologies that are based on alternative natural sources. The methanol-to-olefins (MTO) process is a vital step in the conversion of alternative sources to light olefins: methanol can be made from almost any gasifiable carbonaceous material, following which MTO technology converts methanol to crucial petrochemical feedstock like ethene and propene [1,2]. The production of methanol currently occurs mainly through steam reforming of natural gas or through gasification of coal. The conversion of biomass and waste to methanol is, however, on the rise, mainly because these novel technologies form a closed carbon-cycle and do not depend on the declining fossil fuel reserves. By subsequently applying MTO technology to the methanol produced, one could make almost anything out of methanol that can currently be made out of crude oil.

While several different acidic zeolite and zeotype structures, like HZSM-5 and HSAPO-34 respectively, are well-known MTO catalysts, a major target is the design and development of an ideal MTO catalyst. This material should not only exhibit superior catalytic activity towards olefin formation; it should also suppress the secondary reactions that form alkanes and aromatics and lead to deactivation of the catalyst by coke formation. Most importantly, we aim to control product selectivity, e.g. the ethene/propene ratio, to meet the specific market demands at any given time.

In the search for control of product distribution, a detailed understanding of the MTO reaction mechanism is vital. Quite remarkably, however, the actual mechanism of the conversion of methanol to olefins in acidic zeolites has been a hugely challenging problem for more than 30 years. The main question is how initial C-C coupling occurs from C1 species like methanol and dimethylether (DME). This has led to more than 20 distinct mechanistic proposals with all kinds of reactive intermediates, such as ylides, carbenium ions and radicals [1]. Speculation centered mainly on mechanisms based on the 'direct' formation of small olefins from only methanol, dimethylether and other single-carbon derivates. Recently, however, experimental studies by Haw and co-workers provided evidence that extensively purified methanol is unreactive under regular MTO conditions [3,4]. Our own theoretical results confirmed this controversial statement by showing that methanol alone cannot be coupled directly into hydrocarbons at rates relevant to steady-state conversion [5,6]. In this paper we will give a general discussion of recent developments in the alternative 'hydrocarbon pool' (HP) proposal [7,8]. We will focus on the supramolecular picture developed by Haw et al. [9] and further extend it with new contributions that should be considered when charged intermediates are involved.

2. COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations using the B3LYP functional were performed within the Gaussian03 software package [10,11]. Both the small cluster approach and the two-layered QM/QM embedded ONIOM method were employed. This more advanced method allows for inclusion of the zeolite framework at moderate additional computational cost. Inclusion of the framework is vital when studying the HP route, which is space-demanding and based on carbenium-ion intermediates. The ONIOM method is currently widely used in zeolite chemistry [12-17], as it has been shown to be a very robust method [18]. Furthermore, this method gives results as accurate as those of full periodic calculations [19], but at a significantly lower computational cost [20].

Calculations were performed on aluminosilicates with three industrially and/or academically important topologies: MFI, BEA and CHA [21]. HZSM-5 is an industrially important zeolite exhibiting the medium-pore MFI topology and containing two sets of intersecting channels, each composed of 10-membered rings. Durene is the largest polymethylbenzene that can be fed directly along its narrow channels [22]. The HBeta zeolite (BEA), on the other hand is a large pore zeolite with three sets of intersecting 12-membered ring channels, allowing direct introduction of large molecules such as hexamethylbenzene. It is interesting for mechanistic studies, although not as a commercial catalyst for the MTO process because it cokes up too easily. The silico-aluminophosphate HSAPO-34 exhibits the CHA topology, which is a structure with spacious cages, interconnected by small 8-membered ring windows. Because of their higher complexity, we have not yet modeled any silico-aluminophosphates like HSAPO-34. Instead, we have focused on the aluminosilicate chabazite which has the same CHA topology as HSAPO-34. Generally speaking, the zeolite framework can contain parallel or intersecting channels (like the MFI topology of HZSM-5), cages interconnected by small windows (like the CHA topology of HSAPO-34 and chabazite) or a combination of both cages and channels (like the BEA topology in HBeta).

3. RESULTS AND DISCUSSION

3.1. Failure of direct mechanisms from theoretical viewpoint

In previous work, we showed that all combinations of methanol, DME, framework-bound methoxy groups and water could not lead to any C2 species because of excessively high reaction barriers and exotic intermediates preceding the various often-proposed C-C coupling steps. We tackled the vast number of potential direct mechanisms by setting up an extensive reaction scheme, tying together a large variety of possible direct reactions, even including several previously overlooked pathways. Based on reaction rates at MTO-relevant temperatures we demonstrated that no complete direct pathway from methanol leading all the way to ethene (or to any intermediate containing a carbon-carbon bond) exists [6,23]. The only intermediates that could be directly formed are methane, formaldehyde and the trimethyl oxonium ion.

3.2. Alternative hydrocarbon pool proposal

The most likely alternative to the 'direct' mechanisms is provided by the 'hydrocarbon pool' (HP) proposal, in which organic species trapped in the zeolite pores serve as a platform to which C1 species can attach (e.g. through repeated methylation by methanol), following which internal rearrangements and/or additional methylation leads to splitting off of olefins [7,8]. Further methylation steps would then regenerate the original HP and close the catalytic cycle. By using this organic scaffolding to build the C2 species, the high-energy intermediates proposed in the 'direct' mechanisms can be bypassed. The elementary steps governing this HP process are still not well understood, however, mainly because secondary reactions consume and mask the primary products, severely complicating interpretation of experimental data. Theoretical methods provide an ideal tool to unravel this complex network of reactions, as individual reaction steps can easily be modeled separately. Recent calculations are guided by the general consensus on a hydrocarbon pool consisting mainly of polymethylbenzenes, which have been shown to be active for olefin formation independent of the zeotype catalyst chosen [24-26]. There is also strong experimental evidence for cyclic resonance-stabilized tertiary cations as persistent species in the pores, such as cyclopentenyl and pentamethylbenzenium cations in HZSM-5 [27-28] and hexamethylbenzenium and heptamethylbenzenium (7MB+) cations in HBeta [29-30]. *Gem*-dimethylbenzenium cations in particular have been observed by in situ ^{13}C solid-state NMR in aluminosilicates and form the main starting point from which commonly proposed hydrocarbon pool routes (such as the 'paring' and 'side-chain' mechanisms) originate [31]. The heptamethylbenzenium cation (7MB+), for example, is formed from hexamethylbenzene (HMB) through a one-step geminal methylation by methanol.

3.3. Towards a supramolecular catalyst

Due to the complexity of the HP proposal, Haw et al. suggested that the catalyst should not be considered as a typical acid zeolite framework merely containing certain hydrocarbons, but rather that each cage with all included organic and inorganic species should be seen as a supramolecule [9]. The nature and catalytic behavior of various supramolecular sites for MTO conversion is defined by the complex interplay between the inorganic framework, the organic hydrocarbon pool species and several other factors. Fig. 1 presents an overview of all the separate contributions, which, when combined, will define the active HP species as well as the reaction mechanism and the products that will consequently be formed.

With respect to the inorganic framework, zeolite composition (F1) is a first important factor. Although traditionally aluminosilicates (like HZSM-5) are most often considered, certain zeotype silico-aluminophosphates (like HSAPO-34) also show excellent MTO activity. Furthermore, the silico-aluminophosphate composition leads to a lower, relatively moderate, acidic strength, which has the great advantage of suppressing the secondary reactions. As the HP mechanism is a space-demanding process, pore architecture and shape selectivity will also play a crucial role. The cage dimensions (F2) will define both the maximum volume and shape allowed for bulky molecules. Channel diameters (F3), on the other hand, will control diffusion: small channels or windows will only allow small molecules like methanol/water and ethene/propene to enter and exit the cages, thus providing a basis for both reactant and product shape selectivity.

The organic reaction center (O1) is essential for an active MTO catalyst, as it acts as a platform upon which C-C bonds can be made and broken. Without this platform, C-C coupling can only occur via the direct mechanisms for which rate coefficients are too low. Different organic components will exhibit different activity and different product selectivity, so establishment and modification of this species is crucial towards understanding and obtaining product control. In the case of polymethylbenzenes as an active HP species, for example, increasing the number of methyl groups is believed to significantly decrease the barrier to olefin synthesis, but at the same time to lead also to higher propene selectivity [32].

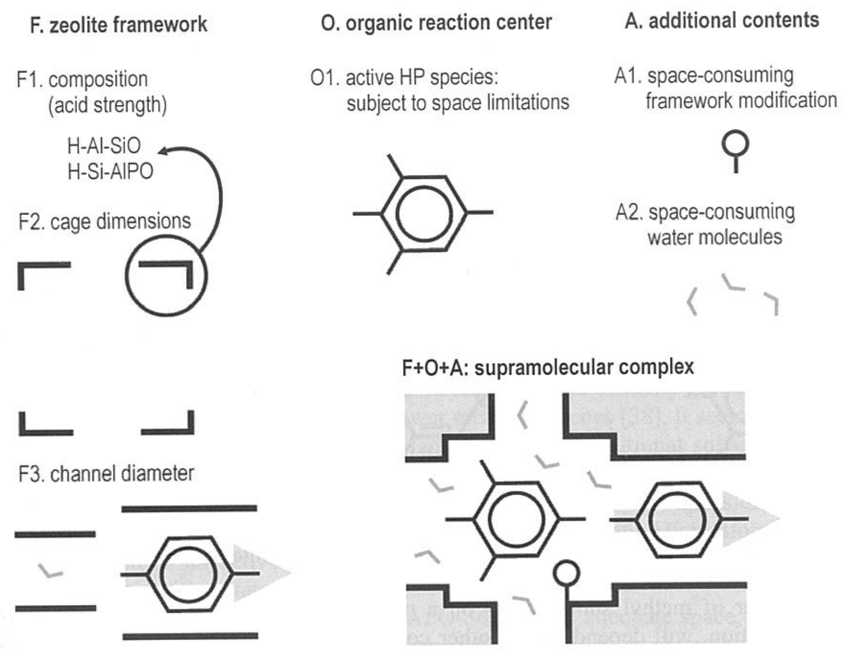

Fig. 1. Separate contributions that create the supramolecular catalyst as suggested by Haw et al. [9]

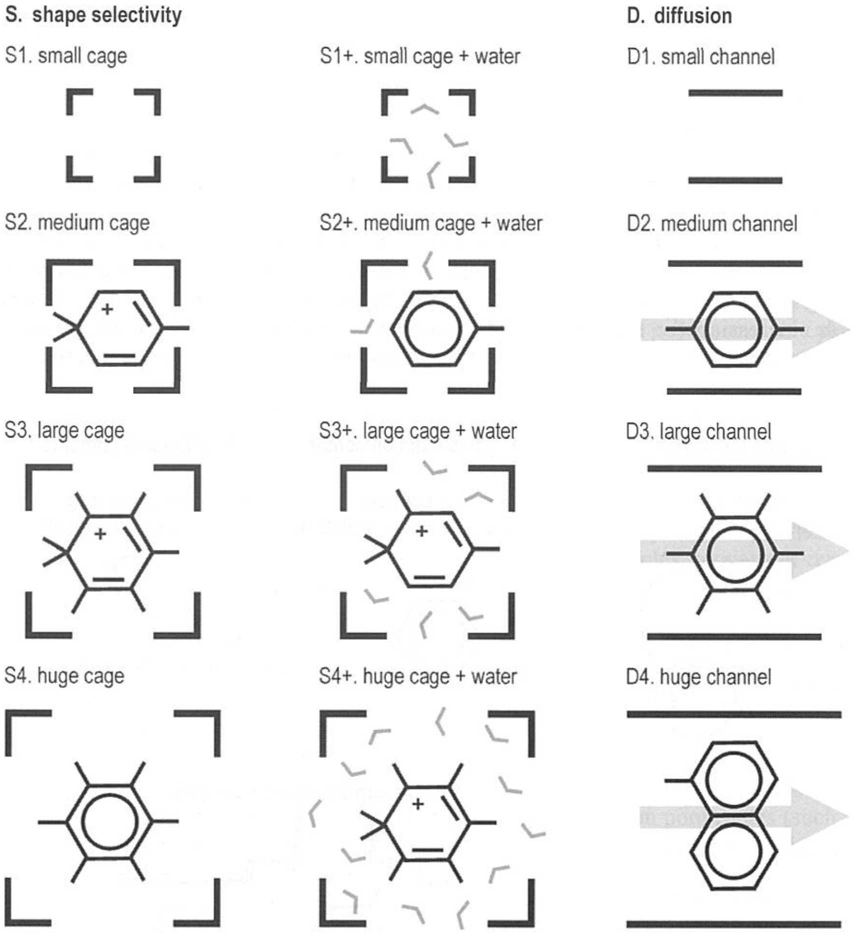

Fig. 2. Most likely intermediates from initiating step depending on zeolite topology.

The number of methyl substitutions on a methylbenzene, and as a consequence also product distribution, will depend on the other contributions shown in Fig. 1. The degree of methylation depends mainly on the available volume, which is determined predominantly by the cage dimensions. The cage dimensions can, however, also be tailored by additional space-consuming contents, such as inorganic framework modification or additional adsorbed molecules. Control of the spatial arrangement of cages with diverse functionality is, therefore, one of the ultimate goals in MTO catalysis. Haw et al. succeeded in applying inorganic post-synthesis modification with tetramethylphosphonium cations to occupy cage volume (A1) [33]. They managed to synthesize a material with slightly reduced catalytic activity, but with a significantly increased selectivity towards ethene. Thus, tailoring the organic component by adding additional inorganic material to some cages through ship-in-a-bottle reactions seems to be a first step towards product control. Essential volume can also be occupied by other molecules. For example, Haw et al. also showed that a higher loading of water leads to a reduction of free volume (A2) [32]. Consequently, only the lower methylbenzenes could act as active HP species and an increase in ethene/propene ratio was observed.

3.4. Failure of direct mechanisms from topological viewpoint

The supramolecular premise of a bulky HP molecule in the zeolite pores shown in Fig. 1 implies that zeolites with very small cages (as illustrated in Fig. 2: S1 and S1+) that are unable to host this space-demanding process, should not demonstrate any MTO activity whatsoever. Recently, Cui et al. put this hypothesis to the test by performing experiments on systematically selected framework structures with varying pore and channel sizes [34]. Their results confirmed that the MTO reaction only takes place on zeolites that allow the hydrocarbon pool mechanism to work, i.e. zeolites with larger cages or zeolites where channel intersections can also serve as an extended space for reactive intermediates. This important experimental verification of small cages providing an inactive MTO catalyst was attributed to transition state shape selectivity. Experimental claims to transition state shape selectivity are, ideally, verified by theoretical methods, since these are more suited for elucidating the extent to which the local shape of the pore influences local reaction rates [35-36]. For the initiating step forming crucial cationic intermediates, the experimental claim to transition state shape selectivity has indeed been confirmed by our theoretical calculations [37], as will be further explained in the following paragraph.

3.5. Cationic intermediates as part of the supramolecule

For a zeolite with medium sized cages, or in the case of MFI medium sized channel intersections, there is inadequate volume for the higher *gem*-dimethylbenzenium cations to be formed (S2). In a recent communication, we have demonstrated that neither the size of the methylbenzene reactant nor that of the *gem*-dimethylbenzenium cation product is crucial, but that the activity of a HP molecule is governed largely by the size of the transition state leading to the geminal methyl group, and as such will be subject to transition state shape selectivity [37]. This theoretical prediction was confirmed when Svelle et al. demonstrated that even though the higher methylbenzenes are present in MFI, they are virtually unreactive and ethene appears to be formed exclusively from the lower methylbenzenes [38]. It seems to us probable that, even for the lower methylbenzenes, a large number of additional solvent molecules or inorganic framework modification would further take up the much-needed space for the transition state to form and further reaction would become almost impossible (S2+). Most importantly, we stress the novel observation that even if an aromatic HP platform is present, it can only perform as an active species for olefin production if the surrounding conditions allow favorable transition states as well.

For a zeolite with larger cages (like HSAPO-34) there is adequate space, not only for the bulky HP species, but also for the transition state leading to heptamethylbenzenium ion formation (S3). Furthermore, as shown in Fig. 3, the encapsulating cage provides ideal electrostatic stabilization of this ion, resulting in a very low barrier to formation of this species [37]. Adding solvent molecules or inorganic features would reduce the amount of methyl substitutions and increase ethene selectivity (S3+), while simultaneously slightly reducing catalytic activity. In a zeolite like HBeta, on the other hand, the cages are too big (S4) to provide the necessary electrostatic stabilization (illustrated in Fig. 3). Although there is enough space for the heptamethylbenzenium ion to be formed, it is relatively unstable with respect to the neutral species. In practice, this will most probably be remedied by solvent molecules like water or methanol (S4+).

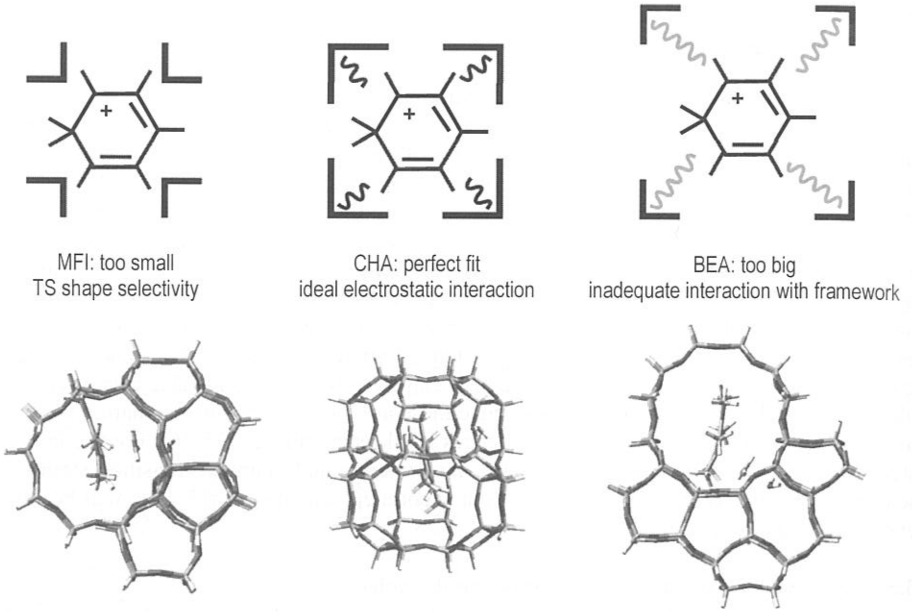

Fig. 3. Refinement of the supramolecular picture: importance of the electrostatic effect of the zeolite topology on the carbenium ion product (top) and transition state shape selectivity (bottom), both for *gem*-methylation of hexamethylbenzene.

3.3. Channel diameter

Not only the cage (or channel intersection) dimensions are important, but also the channel diameters. Very small channels (as in HSAPO-34) in D1 (Fig. 2) will not allow diffusion of any HP species. This means that the HP platform needs to be assembled through a ship-in-a-bottle synthesis in the larger cages. Once the methylbenzene is successfully formed, it remains trapped. This guarantees the crucial combination of an acid site and an active HP molecule in one single cage. However, aromatics will age into larger, less active, aromatic species, until the catalyst is filled with coke and must be regenerated by combustion. Medium sized channels (as in ZSM-5) allow for introduction or diffusion from the lower methylbenzenes (D2), while the higher methylbenzenes remain trapped [22]. If we consider only reactant and product shape selectivity, this would seem an interesting topology demonstrating high activity as well as high propene selectivity. But, because of transition state shape selectivity for the initiating step in HZSM-5, the trapped higher methylbenzenes are virtually unreactive.

Large channels (as in HBeta) on the other hand (D3), will not only allow easy entrance but also an easy exit from the catalyst for the active hydrocarbon pool species. Furthermore, there are no constraints on secondary reactions leading to undesirable larger aromatic species. Methylnaphtalenes, for example, are less reactive HP species than methylbenzenes (D4) and will eventually lead to complete deactivation of the catalyst [9].

4. CONCLUSIONS

In recent developments, both experimental and theoretical work has firmly demonstrated that the frequently suggested direct mechanisms all fail to explain initial C-C coupling in the methanol-to-olefin process. Furthermore, theoretical calculations have clearly illustrated the extent to which the organic hydrocarbon pool species and the inorganic zeolite framework cooperate as a supramolecular catalyst towards alternative pathways. We are currently actively pursuing an entire low-energy pathway linking methanol all the way to ethene.

Both hydrocarbon pool species and zeolite topology play a crucial role in the reaction kinetics for the initial C-C coupling, to the extent that there might not be just one methanol-to-olefin mechanism, but several separate mechanisms tailored to each different zeotype material. The supramolecular picture as developed by Haw et al. has been extended here by stating that not only the traditional concepts of reactant and product shape selectivity need to be taken into account, but that transition state shape selectivity will play a far more important role than either of these. Furthermore, we have illustrated the effect of pore size and shape on the stability and ease of formation for crucial intermediates and have demonstrated the importance of the electrostatic interaction between the cationic intermediate and the zeolite framework.

From here, we need further theoretical insights into the effect of zeolite topology and composition on the entire hydrocarbon pool route. Ideally, we would combine the knowledge obtained from both theory and experiment to create a fine-tuned local spatial environment that optimizes catalytic activity, improves product selectivity and simultaneously suppresses the unwanted secondary reactions.

ACKNOWLEDGEMENTS

This work is supported by the Fund for Scientific Research - Flanders (FWO) and the Research Board of Ghent University.

REFERENCES

[1] M. Stöcker, Microporous Mesoporous Mater. 29 (1999) 3.
[2] J. F. Haw, W. G. Song, D. M. Marcus and J. B. Nicholas, Acc. Chem. Res. 36 (2003) 317.
[3] W. G. Song, D. M. Marcus, H. Fu, J. O. Ehresmann and J. F. Haw, J. Am. Chem. Soc. 124 (2002) 3844.
[4] D. M. Marcus, K. A. McLachlan, M. A. Wildman, J. O. Ehresmann, P. W. Kletnieks and J. F. Haw, Angew. Chem. 118 (2006) 3205; Angew. Chem. Int. Ed. 45 (2006) 3133.
[5] D. Lesthaeghe, V. Van Speybroeck, G. B. Marin and M. Waroquier, Chem. Phys. Lett. 417 (2006) 309.
[6] D. Lesthaeghe, V. Van Speybroeck, G. B. Marin and M. Waroquier, Angew. Chem. 118 (2006) 1746; Angew. Chem. Int. Ed. 45 (2006) 1714.
[7] R. M. Dessau, J. Catal. 99 (1986) 111.
[8] I. M. Dahl and S. Kolboe, J. Catal. 149 (1994) 458.
[9] J. F. Haw and D. M. Marcus, Top. Catal. 34 (2005) 41.
[10]Gaussian 03, Revision B.03, M. J. Frisch et al., Gaussian, Inc., Wallingford CT (2003).
[11]A. D. Becke, J. Chem. Phys. 98 (1993) 5648.
[12]A. Damin, F. Bonino, G. Ricchiardi, S. Bordiga, A. Zecchina and C. Lamberti, J. Phys. Chem. B 106 (2002) 7524.
[13]S. Kasuriya, S. Namuangruk, P. Treesukol, M. Tirtowidjojo and J. Limtrakul, J. Catal. 219 (2003) 320.
[14]M. Boronat, P. M. Viruela and A. Corma, J. Am. Chem. Soc. 126 (2004) 3300.

[15]K. Sillar and P. Burk, J. Phys. Chem. B 108 (2004) 9893.
[16]B. Jansang, T. Nanok and J. Limtrakul, J. Phys. Chem. B 110 (2006) 12626.
[17]D. Lesthaeghe, G. Delcour, V. Van Speybroeck, G. B. Marin and M. Waroquier, Microporous Mesoporous Mater. 96 (2006) 350.
[18]J. T. Fermann, T. Moniz, O. Kiowski, T. J. McIntire, S. M. Auerbach, T. Vreven and M.J. Frisch, J. Chem. Theor. Comput. 1 (2005) 1232.
[19]N. Govind, J. Andzelm, K. Reindel and G. Fitzgerald, Int. J. Mol. Sci. 3 (2002) 423.
[20]X. Solans-Monfort, M. Sodupe, V. Branchadell, J. Sauer, R. Orlando and P. Ugliengo, J. Phys. Chem. B 109 (2005) 3539.
[21]http://www.iza-structure.org/databases/
[22]A. Sassi, M. A. Wildman, H. J. Ahn, P. Prasad, J.B. Nicholas and J. F. Haw, J. Phys. Chem. B 106 (2002) 2294.
[23]D. Lesthaeghe, V. Van Speybroeck, G. B. Marin and M. Waroquier, Ind. Eng. Chem. Res. (2006) in press.
[24]W. Song, J. F. Haw, J. B. Nicholas and C. S. Heneghan, J. Am. Chem. Soc. 122 (2000) 10726.
[25]B. Arstad and S. Kolboe, J. Am. Chem. Soc. 123 (2001) 8137.
[26]U. Olsbye, M. Bjorgen, S. Svelle, K.-P. Lillerud and S. Kolboe, Catal. Today 106 (2005) 108.
[27]T. Xu, D. H. Barich, P. W. Goguen, W. G. Song, Z. K. Wang, J. B. Nicholas and J. F. Haw, J. Am. Chem. Soc. 120 (1998) 4025.
[28]J. F. Haw, J. B. Nicholas, W. Song, F. Deng, Z. Wang, T. Xu and C. S. Heneghan, J. Am. Chem. Soc. 122 (2000) 4763.
[29]M. Bjorgen, F. Bonino, S. Kolboe, K.-P. Lillerud, A. Zecchina and S. Bordiga, J. Am. Chem. Soc. 125 (2003) 15863.
[30]W. G. Song, J. B. Nicholas, A. Sassi and J. F. Haw, Catal. Lett. 81 (2002) 49.
[31]B. Arstad, J. B. Nicholas and J. F. Haw, J. Am. Chem. Soc. 126 (2004) 2991.
[32]W. Song, H. Fu and J. F. Haw, J. Am. Chem. Soc. 123 (2001) 4749.
[33]W. Song and J. F. Haw, Angew. Chem, 115 (2003) 920; Angew. Chem. Int. Ed. 42 (2003) 891.
[34]Z. M. Cui, Q. Liu, W.G. Song and L. J. Wan, Angew. Chem. 118 (2006) 6662; Angew. Chem. Int. Ed. 45 (2006) 6512.
[35]L. A. Clark, M. Sierka and J. Sauer, J. Am. Chem. Soc. 2004, 126, 936.
[36]A. M. Vos, X. Rozanska, R. A. Schoonheydt, R. A. van Santen, F. Hutschka and J. Hafner, J. Am. Chem. Soc. 2001, 123, 2799.
[37]D. Lesthaeghe, B. De Sterck, V. Van Speybroeck, G.B. Marin and M. Waroquier, Angew. Chem. Int. Ed. 47 (2007) 1311.
[38]S. Svelle, F. Joensen, J. Nerlov, U. Olsbye, K.-P. Lillerud, S. Kolboe and M. Bjorgen, J. Am. Chem. Soc. 128 (2006) 14770.