PCCP

Physical Chemistry Chemical Physics

This paper is published as part of a PCCP Themed Issue on:

"Molecules in Confined Spaces: The Interplay between Spectroscopy and Theory to develop Structure-Activity Relationships in the fields of Heterogeneous Catalysis, Sorption, Sensing and Separation Technology"

Guest Editor: Bert Weckhuysen

Editorial Highlight

Editorial Highlight: Molecules in confined spaces
Robert A. Schoonheydt and Bert M. Weckhuysen, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b905015a

Perspectives

Nanoporous oxidic solids: the confluence of heterogeneous and homogeneous catalysis
John Meurig Thomas, Juan Carlos Hernandez-Garrido, Robert Raja and Robert G. Bell, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819249a

Supported vanadium oxide in heterogeneous catalysis: elucidating the structure–activity relationship with spectroscopy
Ilke Muylaert and Pascal Van Der Voort, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819808j

Correlating phase behaviour and diffusion in mesopores: perspectives revealed by pulsed field gradient NMR
Rustem Valiullin, Jörg Kärger and Roger Gläser, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b822939b

Communications

Viscosity sensing in heated alkaline zeolite synthesis media
Lana R. A. Follens, Erwin K. Reichel, Christian Riesch, Jan Vermant, Johan A. Martens, Christine E. A. Kirschhock and Bernhard Jakoby, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b816040f

A small molecule in metal cluster cages: H_2@Mg_n (n = 8 to 10)
Phillip McNelles and Fedor Y. Naumkin, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819479c

Papers

Confinement effects on excitation energies and regioselectivity as probed by the Fukui function and the molecular electrostatic potential
Alex Borgoo, David J. Tozer, Paul Geerlings and Frank De Proft, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b820114e

Rotation dynamics of 2-methyl butane and *n*-pentane in MCM-22 zeolite: a molecular dynamics simulation study
Shiping Huang, Vincent Finsy, Jeroen Persoons, Mark T.F. Telling, Gino V. Baron and Joeri F.M. Denayer, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819334g

Reactivity in the confined spaces of zeolites: the interplay between spectroscopy and theory to develop structure–activity relationships for catalysis
Mercedes Boronat, Patricia Concepción, Avelino Corma, María Teresa Navarro, Michael Renz and Susana Valencia, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b821297j

The influence of the chemical compression on the electric properties of molecular systems within the supermolecular approximation: the LiH molecule as a case study
Anna Kaczmarek and Wojciech Bartkowiak, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819346k

Multinuclear gallium-oxide cations in high-silica zeolites
Evgeny A. Pidko, Rutger A. van Santen and Emiel J. M. Hensen, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b815943b

Metal–organic frameworks as high-potential adsorbents for liquid-phase separations of olefins, alkylnaphthalenes and dichlorobenzenes
Luc Alaerts, Michael Maes, Monique A. van der Veen, Pierre A. Jacobs and Dirk E. De Vos, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b823233d

Tetramethyl ammonium as masking agent for molecular stencil patterning in the confined space of the nano-channels of 2D hexagonal-templated porous silicas
Kun Zhang, Belén Albela, Ming-Yuan He, Yimeng Wang and Laurent Bonneviot, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819872c

Photovoltaic activity of layered zirconium phosphates containing covalently grafted ruthenium tris(bipyridyl) and diquat phosphonates as electron donor/acceptor sites
Laura Teruel, Marina Alonso, M. Carmen Quintana, Álvaro Salvador, Olga Juanes, Juan Carlos Rodriguez-Ubis, Ernesto Brunet and Hermenegildo García, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b816698f

The characterisation and catalytic properties of biomimetic metal–peptide complexes immobilised on mesoporous silica
Gerhard D. Pirngruber, Lukas Frunz and Marco Lüchinger, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819678h

Physisorption and chemisorption of alkanes and alkenes in H-FAU: a combined *ab initio*–statistical thermodynamics study
Bart A. De Moor, Marie-Françoise Reyniers and Guy B. Marin, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819435c

Accelerated generation of intracrystalline mesoporosity in zeolites by microwave-mediated desilication
Sònia Abelló and Javier Pérez-Ramírez, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b819543a

Regio- and stereoselective terpene epoxidation using tungstate-exchanged takovites: a study of phase purity, takovite composition and stable catalytic activity
Pieter Levecque, Hilde Poelman, Pierre Jacobs, Dirk De Vos and Bert Sels, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b820336a

Probing the microscopic hydrophobicity of smectite surfaces. A vibrational spectroscopic study of dibenzo-*p*-dioxin sorption to smectite
Kiran Rana, Stephen A. Boyd, Brian J. Teppen, Hui Li, Cun Liu and Cliff. T. Johnston, *Phys. Chem. Chem. Phys.*, 2009
DOI: 10.1039/b822635k

Theoretical evaluation of zeolite confinement effects on the reactivity of bulky intermediates†‡

David Lesthaeghe, Veronique Van Speybroeck* and Michel Waroquier

Received 5th February 2009, Accepted 8th April 2009
First published as an Advance Article on the web 14th May 2009
DOI: 10.1039/b902364j

Zeolites provide a unique setting for heterogeneous Brønsted acid catalysis, because the effects of the surrounding framework on fundamental reaction kinetics go well beyond what would be expected for a mere reaction flask. This aspect becomes very pronounced when bulky molecules form key intermediates for the reaction under study, which is exactly when the interaction between the framework and the intermediate is maximal. We will use the example of methanol-to-olefin conversion (MTO), and, more specifically, the constant interplay between the inorganic host framework and the organic hydrocarbon pool co-catalyst, to illustrate how zeolite confinement directly influences catalytic reaction rates. Theoretical calculations are used to isolate and quantify these specific effects, with the main focus on methylbenzenes in ZSM-5, as the archetypical MTO catalyst. This review intends to give an overview of recent theoretical insights, which have proven to provide an ideal complementary tool to experimental investigations. In addition, we will also introduce the role of zeolite breathing in activating a catalytic cycle.

Introduction

Dwindling oil reserves and the rapidly increasing demand for oil-based chemicals call for the development of new technologies based on alternative natural sources, such as the methanol-to-olefins (MTO) technology. For over 30 years the actual mechanism of the MTO process in acidic zeolites was the source of considerable debate, fuelled by countless and often conflicting propositions.[1] Possible direct mechanisms, in which methanol or small methanol derivatives co-react to form the initial C–C bond, have since all been shown to fail, both from an experimental[2–4] and theoretical[5] viewpoint. The currently accepted hydrocarbon pool model successfully provides a means towards olefin production with lower energy barriers, bypassing the problematic direct reaction routes. In this hypothesis, organic molecules that are already present in the pores act as co-catalysts towards olefin formation, as shown in Fig. 1.[6,7] These hydrocarbon pool compounds (which could be any organic molecule) are methylated by methanol, after which internal rearrangements occur and finally lead to the splitting off of light olefins (a specific example will be discussed in greater detail later in this article). Typically, methylbenzenes have been considered as active

Center for Molecular Modeling, Proeftuinstraat 86, 9000, Ghent, Belgium. E-mail: david.lesthaeghe@ugent.be, veronique.vanspeybroeck@ugent.be; Fax: +32 (0)9 264 66 97; Tel: +32 (0)9 264 65 64

† This article was submitted as part of a Themed Issue on molecules in confined spaces. Other papers on this topic can be found in issue 16 of vol. 11 (2009). This issue can be found from the *PCCP* homepage [http://www.rsc.org/pccp]

‡ In honour of the retirement of Professor Robert A. Schoonheydt of the Catholic University of Leuven (Belgium).

David Lesthaeghe

David Lesthaeghe obtained his MS degree in engineering physics at Ghent University, Belgium with highest honour. He received his PhD in Engineering in 2007 at the same university, studying acid-catalysed reactions in zeolites using quantum chemical methods. He is currently an FWO post-doctoral fellow at the Center for Molecular Modeling, presently involved in the theoretical modelling of methanol-to-olefin conversion and zeolite synthesis.

Veronique Van Speybroeck

Veronique Van Speybroeck graduated as a civil engineer in physics at Ghent University in 1997 and received her PhD in 2001 at the same university on a subject dealing with theoretical simulations of chemical reactions with static and dynamical approaches. Afterwards she was granted a postdoctoral fellowship from the National Fund for Scientific Research Flanders and spent several short visits in foreign institutes. In 2007 she became a Research Professor at the Ghent University. Her current research focuses on first principle chemical kinetics in nanoporous materials.

 This journal is © the Owner Societies 2009

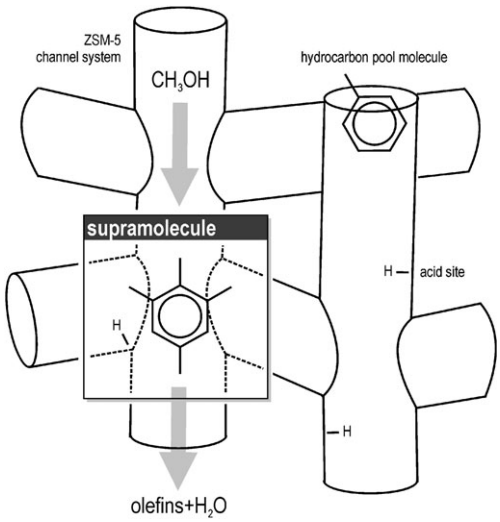

Fig. 1 Methanol-to-olefin conversion in ZSM-5. The catalyst consists of a local area of the zeolite framework with at least one Brønsted acid site and an organic co-catalyst, like a methylbenzene.

hydrocarbon pool compounds,[8–10] yet suggestions of smaller compounds such as propene have also surfaced in the last couple of years, especially for zeolites with limited space available like ZSM-5.[11] The combination of the co-catalytic organic component inside the inorganic catalyst framework creates a rather unique catalyst as illustrated in Fig. 1, which seems supramolecular in nature. Crucial parameters for MTO conversion are, therefore, not restricted to framework topology, framework composition or acid site strength, but also include size, shape and orientation of the hydrocarbon pool compound.

Only recently have we been able to construct a complete catalytic cycle, combining both theoretical and experimental results.[12] Our results show that the organic hydrocarbon pool species and the inorganic zeolite framework have to cooperate towards low-energy alternative pathways. Theoretical calculations like these have proven to provide additional insight to experimental work. In this paper we will revisit and highlight the nature of this cooperation, bringing together theoretical results scattered over several sources, and will also introduce the role of zeolite breathing in a complete catalytic cycle. A thorough review of experimental studies is beyond the scope of this purely theoretical review, for which we refer to ref. 1 and 8.

Michel Waroquier

Michel Waroquier is full professor in physics at Ghent University. In 1997 he left his former research area in theoretical nuclear physics to start up a molecular modeling division basing on his expertise on many-body problems. He succeeded in building his team up to more than 20 people, mainly physicists. The current research areas cover nanozporous materials, (synthesis, chemical kinetics...), materials physics, spectroscopy (EPR, NMR, IR, Raman). His main interest is in model development and validation of the new models in computational applications.

Results and discussion

We first bring together results and discuss issues related to electrostatic stabilisation, space limitations and rotational mobility, before turning to the role of zeolite breathing.

Electrostatic stabilisation

Electrostatic interactions are especially important for protonated intermediates, as such cationic species typically interact with the surrounding framework atoms. The positively charged silicon atoms are somewhat screened by the oxygen tetrahedron, but the bridging oxygen atoms are free to interact with a cation while the net negative charge is known to be easily spread out over the framework.[13,14] Furthermore, the framework oxygen bridges show a remarkable flexibility to adapt to nearby molecules. The negative shell of oxygen atoms provides a diffuse electron cloud over the inner surface regions, ideally suited to stabilizing cationic species caught in the pores. From a modeling perspective, this is why the framework oxygen should preferably not be described just by classical point charges, but rather by an electron cloud that shifts and adapts to the bulky cation close by.

Certain intermediates, such as the trimethyl oxonium ion can persist as stable species. By systematically incorporating larger chunks of the zeolite framework in our calculations, we have demonstrated that the zeolite framework is necessary to stabilise these ions up to an additional 80 kJ mol^{-1}.[15] Other cationic intermediates, such as carbenium ions, might have a choice presented to them: they may either remain in the pore as stable carbenium ions, with the added advantage of slight flexibility (yet limited by the charge constraints) or form an alkoxide intermediate. Methoxide and ethoxide species are sometimes even believed to be reaction intermediates for MTO conversion, yet this topic is still under considerable debate.[16,17] For small cationic species an alkoxide intermediate will be stable, even at elevated temperatures, but this pattern shifts when larger carbenium ions are considered[18] or when cyclic resonance provides additional stabilization.[19,20] For bulky intermediates, the size and shape of the framework will also assist in the stabilisation. Finally, the presence of alkoxide intermediates rather than carbenium ions has a direct effect on reactivity: key reaction steps will occur either stepwise (through an alkoxide intermediate) or concerted.

The effect of the framework is best illustrated for the formation of a heptamethylbenzenium ion from hexamethylbenzene and methanol. Fig. 2 illustrates this for three topologies: CHA (SSZ-13), BEA (zeolite β) and MFI (ZSM-5). The CHA topology of SSZ-13 (rather large cages with small windows) forms a nice fit and provides adequate interaction between the carbenium ion and the oxygen shell to lower the relative energy by 100 kJ mol^{-1}.[21] Since the windows are too small for such large molecules to enter the cages, they are formed through a ship-in-a-bottle like procedure, and

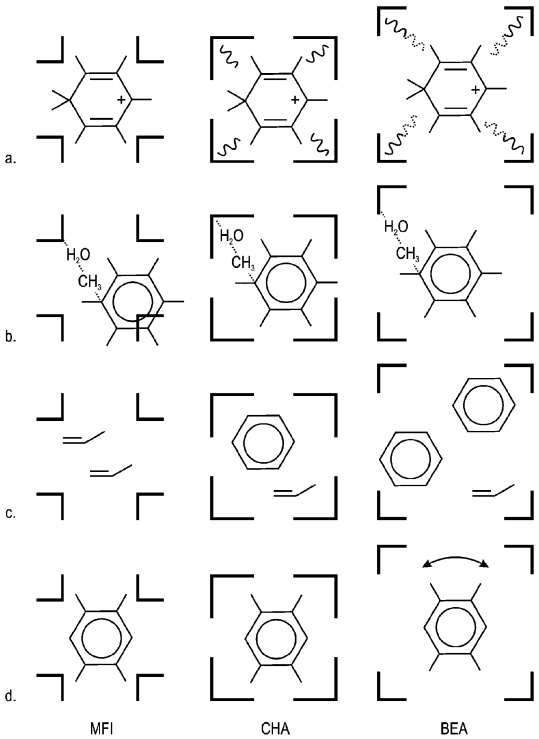

Fig. 2 Conceptual illustration of the influence of framework topology on key concepts.

subsequently cannot leave the cage. The cages and windows of zeolite β (BEA) on the other hand are too big and no such effect is observed, as illustrated in Fig. 2a, while the channel intersections of ZSM-5 are too small to house the hepta-methylbenzenium ion properly. In this last case though, the disproportionality is such that transition state shape selectivity will occur.

Space limitations and shape selectivity

When looking at the full catalytic cycle in Fig. 3, we observed that the slowest steps in this cycle are the initial *gem*-methylation steps, leading to a higher methylbenzene.[12,21–23] Once such an additional methylation occurs on an already methylated position, much faster intramolecular rearrangements occur, such as contraction to a 5-ring, splitting off of isobutene and expansion to a 6-ring.

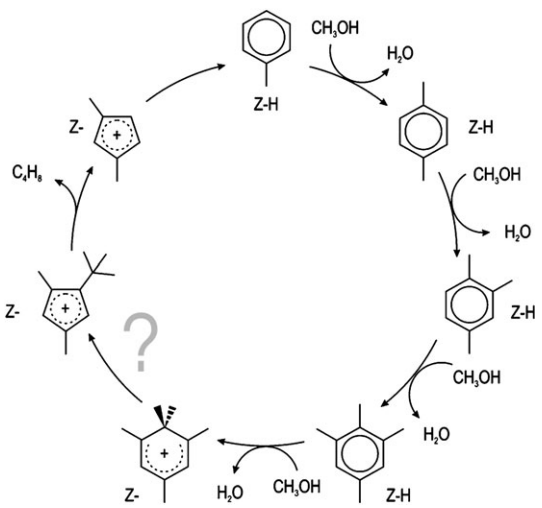

Fig. 3 Full catalytic cycle for MTO conversion.

When this kind of bulky transition state is investigated, it is clear from Fig. 2b how transition state shape selectivity might occur. If the available space is too small (as in the MFI structure of ZSM-5), transition state shape selectivity will result in a higher activity of the lower methylbenzenes rather than the usually more productive higher methylbenzenes, as confirmed by both theoretical and experimental findings.[11,21] This also highlights one of the major differences between the methylbenzene route and the recently suggested propene route in ZSM-5.[11] The methylbenzene route operates under space-limiting conditions whereas the propene route would not, as shown in Fig. 2c, providing a clue as to why the propene route would be competitive in ZSM-5, but not in SAPO-34 or β.

The space limitations also have an effect on the types of reactions. Breaking up larger molecules into smaller ones will be promoted. Reactions requiring limited space might be favoured over those that require more space for example, the paring route (which has a 6-to-5 contraction step leading to olefin elimination as illustrated in Fig. 3) might be favoured over the side-chain route (during which the 6-membered ring is maintained and olefin production occurs on a side chain).[12,24] Space limitations have even been used to block hydrocarbon pool reactivity altogether, by using zeolites that have small channels.[4]

Rotational mobility

Another problem occurs when multi-site reactivity is required. A bulky molecule is restricted to undergoing reactions at just one end, as mobility decreases and rotations through 180 degrees become increasingly difficult with size. If an intermediate needs to flip to the acid site this can only occur within zeolites with larger cages, as illustrated in Fig. 2d.

In most zeolites, there are multiple acid sites in the framework. However, for a cationic intermediate, the additional Brønsted acid proton is of no use since multiple protonation to create a doubly charged cation is rather improbable. Deprotonation must occur prior to a new protonation attempt. This also has an effect on the rigidity of cations: they tend to stay put near the aluminium charge defect, which also has its effect on reactivity. For side-chain growth, for example, the formation of an exocyclic double bond will be more plausible in the *ortho*-position with respect to the *gem*-methyl groups rather than the *para* position, as is most commonly presented.[24]

Framework breathing

Framework breathing is already known to be important for diffusion:[25,26] the flexible framework allows for distortions on the time-scale of diffusion and assists long and bulky molecules somewhat like a peristaltic pump. However, we have found this breathing motion to be important for certain reactions as well. If we consider the paring cycle as in Fig. 3, we see gradual growth of the hydrocarbon pool compound. Adding additional methyl groups, forces the zeolite framework to expand so it can accommodate the ever-bulkier

 This journal is © the Owner Societies 2009

molecule. We have seen, for example, that adding extra methyl groups to penta- and hexamethylbenzene already puts quite significant strain on the ZSM-5 framework.[21] This strain might be the driving force behind the contraction from a 6-ring to a 5-ring, highlighted with a question mark in Fig. 3. After this contraction step, the olefin is split off, reducing the size of the molecule once more. The reduced 5-ring can then expand into the original 6-ring, smaller and more suited to the size and shape of the channel intersection. A full breathing cycle, whereby the zeolite framework expands to accommodate larger methylbenzenes and then contracts when a 5-membered ring is formed and olefins are split off, would correspond to a complete catalytic cycle like the one in Fig. 3, consisting of a multitude of reactions.

The contraction step in Fig. 3 can occur through 2 possible pathways. A direct contraction step, as reported in,[12] or a two-step pathway, during which an alkoxide is formed first. The formation of this alkoxide, as illustrated in Fig. 4, already allows the hydrocarbon pool species to take up significantly less room in the cage. The energy barriers for a relatively small hydrocarbon pool molecule (reaction 1) and a much bulkier species (reaction 2) are shown in Table 1. There is an enormous difference in the total energy barrier: 160.7 *vs.* 6.7 kJ mol^{-1}. While for the heptamethylbenzenium ion a significant contribution of approximately 50 kJ mol^{-1} is given by the active site and the hydrocarbon pool molecule itself, the largest contribution is given by the framework relaxation of −80 kJ mol^{-1}. This indicates that the energy previously stored in the framework during over-methylation to form the heptamethylbenzenium ion, could be consequently released for the olefin-producing contraction step.

Modifications

All these effects can be steered by applying modifications to the system. A first step would be modifying the framework. This can be achieved by attaching organic groups to the lattice, thereby artificially reducing the cavity's size, steering reactivity towards smaller hydrocarbon pool compounds and directly influencing ethene/propene selectivity. Alternatively it can be achieved by incorporating bridging organic groups into the framework, allowing a change from concerted to stepwise mechanisms, where the promotion of alkoxide formation influences the balance.[27,28]

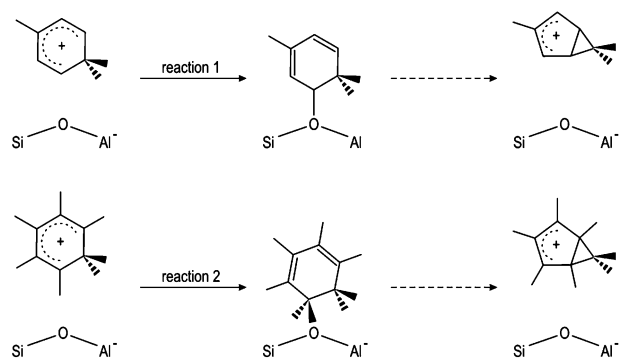

Fig. 4 Two-step pathway for 6-to-5-ring contraction, with the formation of an intermediate alkoxide species.

Table 1 Energy breakdown for the reaction barrier of the reactions shown in Fig. 4 as obtained from standard ONIOM calculations, performed at the B3LYP/6-31+g(d):MNDO level of theory in an 8T:46T ZSM-5 cluster. HP = hydrocarbon pool molecule

Reaction 1	ΔE_0/kJ mol^{-1}
A. Low-level energy of low-level region	20.4
B. High-level energy of 8T active site + HP	140.3
Total barrier = A + B	160.7
Reaction 2	
A. Low-level energy of low-level region	−84.3
B. High-level energy of active site + HP	91.1
Total barrier = A + B	6.7

The zeolite feed can also be modified. Stronger methylating agents might provide a quicker route to higher methylbenzenes, but often these are bulky molecules. Our calculations have shown that, because of transition state shape selectivity, modifying the feed by adding bulky methylating agents does not help. The ideal methyl sources remain methanol and the halomethanes, mainly because these sources require only limited space.[29]

Conclusions

In this article, we have given an overview of all our previously scattered theoretical findings on how zeolite confinement effects influence the reactivity of bulky molecules in the methanol-to-olefin process. Electrostatic stabilisation by the framework oxygen atoms is found to be crucial when cationic intermediates are involved, yet will depend highly on how the size and shape of the cation fits with the size and shape of the zeolite cavities. Space limitations and transition state shape selectivity will define which hydrocarbon pool species will be most reactive within certain zeolites. Flexibility and rotational mobility will define which types of reactions will be possible, and whether multiple sites of the hydrocarbon pool molecule will play an active role.

Finally, we have proposed the hypothesis that framework breathing might not only be important for diffusion of larger molecules, but could also be the driving factor behind ring-contraction steps. Additional research is currently being performed to further quantify this effect.

References

1 M. Stöcker, *Micropor. Mesopor. Mater.*, 1999, **29**, 3–48.
2 W. G. Song, H. Fu and J. F. Haw, *J. Am. Chem. Soc.*, 2001, **123**, 4749–4754.
3 D. M. Marcus, K. A. McLachlan, M. A. Wildman, J. O. Ehresmann, P. W. Kletnieks and J. F. Haw, *Angew. Chem., Int. Ed.*, 2006, **45**, 3133–3136.
4 Z. M. Cui, Q. Liu, W. G. Song and L. J. Wan, *Angew. Chem., Int. Ed.*, 2006, **45**, 6512–6515.
5 D. Lesthaeghe, V. Van Speybroeck, G. B. Marin and M. Waroquier, *Angew. Chem., Int. Ed.*, 2006, **45**, 1714–1719.
6 R. M. Dessau, *J. Catal.*, 1986, **99**, 111–116.
7 I. M. Dahl and S. Kolboe, *J. Catal.*, 1994, **149**, 458–464.
8 J. F. Haw, W. G. Song, D. M. Marcus and J. B. Nicholas, *Acc. Chem. Res.*, 2003, **36**, 317–326.
9 B. Arstad, J. B. Nicholas and J. F. Haw, *J. Am. Chem. Soc.*, 2004, **126**, 2991–3001.

10 M. Bjorgen, U. Olsbye, D. Petersen and S. Kolboe, *J. Catal*., 2004, **221**, 1–10.
11 S. Svelle, F. Joensen, J. Nerlov, U. Olsbye, K.-P. Lillerud, S. Kolboe and M. Bjorgen, *J. Am. Chem. Soc*., 2006, **128**, 14770–14771.
12 D. M. McCann, D. Lesthaeghe, P. W. Kletnieks, D. R. Guenther, M. J. Hayman, V. Van Speybroeck, M. Waroquier and J. F. Haw, *Angew. Chem., Int. Ed*., 2008, **47**, 5179–5182.
13 E. M. Morales, C. M. Zicovich-Wilson, J. E. S. Sanchez and L. J. Alvarez, *Chem. Phys. Lett*., 2000, **327**, 224–229.
14 R. Fricke, H. Kosslick, G. Lischke and M. Richter, *Chem. Rev*., 2000, **100**, 2303–2405.
15 D. Lesthaeghe, V. Van Speybroeck, G. B. Marin and M. Waroquier, *Chem. Phys. Lett*., 2006, **417**, 309–315.
16 Y. J. Jiang, W. Wang, V. R. R. Marthala, J. Huang, B. Sulikowski and M. Hunger, *J. Catal*., 2006, **238**, 21–27.
17 J. F. Haw, D. M. Marcus and P. W. Kletnieks, *J. Catal*., 2006, **244**, 130–133.
18 M. Boronat, P. M. Viruela and A. Corma, *J. Am. Chem. Soc*., 2004, **126**, 3300–3309.
19 J. B. Nicholas and J. F. Haw, *J. Am. Chem. Soc*., 1998, **120**, 11804–11805.
20 M. Bjørgen, F. Bonino, S. Kolboe, K.-P. Lillerud, A. Zecchina and S. Bordiga, *J. Am. Chem. Soc*., 2003, **125**, 15863–15868.
21 D. Lesthaeghe, B. De Sterck, V. Van Speybroeck, G. B. Marin and M. Waroquier, *Angew. Chem., Int. Ed*., 2007, **46**, 1311–1314.
22 A. M. Vos, X. Rozanska, R. A. Schoonheydt, R. A. van Santen, F. Hutschka and J. Hafner, *J. Am. Chem. Soc*., 2001, **123**, 2799–2809.
23 A. M. Vos, K. H. L. Nulens, F. De Proft, R. A. Schoonheydt and P. Geerlings, *J. Phys. Chem. B*, 2002, **106**, 2026–2034.
24 D. Lesthaeghe, A. Horré, V. Van Speybroeck, G. B. Marin and M. Waroquier, to be submitted to *Chem.–Eur. J*., 2009.
25 E. G. Derouane, J. B. Nagy, C. Fernandez, Z. Gabelica, E. Laurent and P. Maljean, *Appl. Catal*., 1988, **40**, L1–L10.
26 N. E. R. Zimmermann, S. Jakobtorweihen, E. Beerdsen, B. Smit and F. J. Keil, *J. Phys. Chem. C*, 2007, **111**, 17370–17381.
27 D. Lesthaeghe, V. Van Speybroeck and M. Waroquier, *J. Am. Chem. Soc*., 2004, **126**, 9162–9163.
28 D. Lesthaeghe, G. Delcour, V. Van Speybroeck, G. B. Marin and M. Waroquier, *Micropor. Mesopor. Mater*., 2006, **96**, 350–356.
29 D. Lesthaeghe, S. Malengreaux, V. Van Speybroeck and M. Waroquier, to be submitted to *J. Am. Chem. Soc*., 2009.

 This journal is © the Owner Societies 2009