

## DSM Science & Technology Awards 2007

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## 1 Summary of the candidate's work

### **Unraveling the Reaction Mechanism of Industrial Processes in Zeolite Catalysis: a Quantum Chemical Approach**

**David Lesthaeghe**

#### **Introduction**

Even though acidic zeolites form crucial catalysts for many petrochemical processes, much of their fundamental reactive behavior is only superficially understood. Most often, catalysts are proposed on an 'ad hoc' basis, without a detailed understanding of their functioning on an atomic scale. For very complex reaction networks, it can indeed be difficult, or even impossible, to identify the elementary steps from a purely experimental basis. For those cases where experimental results are ambiguous, quantum chemical molecular modeling techniques provide an excellent complementary tool to laboratory data. This relatively new field of research has seen an enormous surge in popularity, mainly because of the rapid increase in computer power and the development of sufficiently accurate theoretical methods.

From a practical viewpoint, quantum chemical modeling of gas-phase reactions is relatively straightforward, while this is certainly not the case for modeling of zeolites: special attention needs to be given to the model space approximations that are necessary for such extended systems. Firstly, chemical reactions need to be modeled by computationally very demanding quantum chemical methods if we are to describe the changes in electronic binding pattern appropriately. Different approximations are possible, with an increase in accuracy usually accompanied by an increase in computational cost. Secondly, since zeolites are extended materials with a large number of atoms, a complete and accurate quantum chemical description of the entire system is not only extraordinarily demanding but also, at the moment at least, sim-

ply impossible. This issue has, however, led to the development recently of some advanced techniques that do allow an accurate description of at least the chemically active part of the system. The surrounding environment is included by using a less accurate but faster quantum chemical approximation method.

The candidate has made maximum use of these state-of-the-art techniques in his investigation of two major aspects of zeolite catalysis. In the first part of his research he has focused on the unraveling of complex reaction networks for industrially important processes, like the conversion of methanol to olefins, while in the second part he has investigated how organic modifications to the zeolite framework alter and improve the catalytic properties.

### **The methanol-to-olefin process**

Light olefins, which are traditionally obtained by steam cracking of crude oil fractions, are vital components in the petrochemical industry. However, because the world's finite oil reserves will not be able to meet the ever-increasing demand for oil-based chemicals (and polyolefins in particular), developments currently focus on technologies that are based on alternative natural sources [1]. In the conversion of raw materials to polyolefins, the methanol-to-olefins (MTO) process is a crucial step: methanol can be made from almost any gasifiable carbonaceous material, following which MTO technology converts methanol to crucial petrochemical feedstock like ethene and propene [2]. Natural gas is the current main source for methanol production (making great use of otherwise stranded natural gas reserves), but conversion of biomass and/or waste to methanol permits a future shift in emphasis from finite to renewable resources. By subsequently applying MTO technology to the methanol produced, one could make almost anything that can currently be made out of crude oil! The latest trends in the price of oil demonstrate how, in the very near future, natural gas will have to act as a bridge between the current oil-based economy and one based on renewable resources. At the moment, therefore, the MTO process is highly topical and considered one of the most important emerging technologies in the production of chemicals.

In stark contrast to its increasing importance, the mechanism of the MTO process has baffled many prominent researchers, mainly because the answer was not to be found in the most obvious places. Quite remarkably, the actual mechanism has been a hugely challenging and highly debated problem for more than 30 years [2]. Until recently, much remained uncertain and the

literature was replete with different and often conflicting propositions. The tricky question was how the initial C-C coupling occurs from C1 species like methanol and dimethyl ether (DME). Speculation centered mainly on mechanisms based on the 'direct' formation of small olefins from only methanol, DME and other single-carbon derivatives. Recently, however, experimental studies suggested that extensively purified methanol might be unreactive under standard MTO conditions [3], which is in complete disagreement with the direct mechanism proposals. This experimental observation was deemed highly controversial and received a lot of criticism by the Establishment at the time. A viable, yet more complex alternative to the direct mechanisms, however, is given by the 'hydrocarbon pool' model [4], in which some kind of hydrocarbon species trapped in the zeolite pores acts as a co-catalyst towards olefin formation. Lately, this proposal has systematically gained in experimental support, though it is still far from universally accepted. To the MTO research community, it remained unclear if and why the numerous direct mechanisms proposed fail to explain consistent formation of ethene. Furthermore, the elementary reaction steps in the hydrocarbon pool model and the effect of the zeolite environment upon them were barely understood.

In his PhD thesis, the candidate used quantum chemical calculations to finally provide some desperately needed clarity on this issue. The whole class of direct mechanisms, for which initial C-C coupling is taken to occur from C1 species only, was intensively investigated [5, 6]. Earlier theoretical studies tended to be fragmentary, typically investigating only a single reaction step rather than a complete pathway [7]. Nevertheless, the existence of these individual reaction steps was often considered theoretical evidence for the direct proposal, even though no one had succeeded in defining a complete low-energy pathway from methanol to ethene. To resolve this complex issue, the candidate constructed an extensive and consistent reaction scheme, including all the possible pathways and their constituent elementary reaction steps. By combining the individual steps, it was demonstrated on the basis of reaction rate coefficients that the direct mechanism concept can never provide the initial C-C coupling [6]. At the same time, the major bottleneck reactions could also be identified. As this theoretical result marked the end of a long-term research direction, it is considered one of the most influential theoretical results in the entire field of heterogeneous catalysis.

Any alternative proposal, like the up-and-coming 'hydrocarbon pool' hypothesis, needs to provide C-C coupling steps that circumvent these bottlenecks. The hydrocarbon pool model states principally that organic species trapped in the zeolite pores serve as building platforms, to which C1 species can at-

tach methyl groups. The methylated species subsequently undergoes specific rearrangements and/or additional methylation steps, to finally split off light olefins. The original molecule is then regenerated by additional methylation steps. This way, the highly activated steps of the direct mechanisms might be bypassed. In the candidate's PhD thesis, the initiating methylation step (and at the same time C-C coupling step) was investigated [8]. The results shed new light on the role of the zeolite framework as the organic species and the inorganic zeolite cooperate as a supramolecular catalyst [9]. The existing supramolecular picture was extended by the explicit inclusion of previously omitted aspects like transition state shape selectivity and electronic stabilization of vital cationic intermediates by the zeolite framework [8]. From these theoretical results it became clear that the zeolite is much more than a mere shape-selective container with acid sites, since electronic embedding plays a crucial role as well. Detailed insight into the hydrocarbon pool proposal has modernized the current view of the fundamental catalytic nature of the zeolite and its contents.

## Organic functionalized zeolites

Additional insight into the hydrocarbon pool hypothesis is no mere academic goal, but it is required for a guided optimization of the supramolecular catalyst. The most recent efforts in extending the range of applications for structured microporous as well as mesoporous silicates include the creation of a whole new class of catalysts, the so-called 'zeozymes'. By incorporating well-chosen organic fragments directly into the inorganic zeolite framework it might be possible to combine the properties of zeolites with those of enzymes. Over the last couple of years this field has exploded, culminating in numerous functional mesostructures that have been synthesized successfully [10, 11]. However, the number of papers reporting the synthesis of these novel materials exceeds by far those actually investigating the abundantly suggested (and often seemingly promising) applications in catalysis. A detailed understanding of how these novel materials differ from traditional materials is essential for the next step of putting them to practical use. Especially on the nano-scale, theoretical calculations can provide much-needed insights into how the organic groups control fundamental properties, over and above the insights provided by experiments.

Efforts to incorporate organic sites into the structure of zeolites have not been as successful as those to incorporate similar groups into mesoporous materials. For example, first attempts using organosilanes with pendant organic

groups during zeolite synthesis succeeded in attaching phenethyl groups into zeolite structures covalently bonded to framework silicon atoms [12]. Even though a significant advance regarding possible applications was made, the rather large organic groups tended to stick out of the framework, consequently blocking the molecular-sized pores. This problem of pore clogging can only be eliminated by incorporating significantly smaller organic fragments. In the candidate's PhD thesis, two such smaller modifications to zeolite structures (methylene and amine moieties) were theoretically investigated.

The methylene moiety is one of the simplest organic groups that fits perfectly as a bridge between two silicon atoms to form the functional Si-CH<sub>2</sub>-Si group. Even though such mesoporous organo-silicate materials have been successfully synthesized before [13], only recently has a research team been able to synthesize methylene-substituted alumino-silicate zeolites [14]. They failed to explain the observed framework defects, though, like the presence of end-standing Si-CH<sub>3</sub> groups. In the candidate's thesis, the influence of the methylene moiety on fundamental adsorption properties was discussed for both neutral probe molecules and charge compensating cations. Additionally, it was demonstrated that the combination of tetrahedral aluminum atoms (plus a Brønsted acid proton) with a methylene moiety will inevitably lead to protonation of the organic group and subsequent cleavage of the framework [15]. Therefore, it will be extremely difficult to synthesize both microporous and mesoporous methylene-functionalized structured silicates containing aluminum sites.

For similar amine-functionalized zeolites [16], the candidate also showed that even though protonation of the amine group is favorable, this does not necessarily lead to cleavage of the zeolite structure. Furthermore, Si-NH-Si moieties will provide additional basic sites, comparable to traditional Al-O-Si sites but not constrained to the aluminum tetrahedron [17]. This enables more proton locations as well as the possibility of more favorable transition state geometries. This results directly in a drastic reduction in energy barrier for those reactions which would otherwise have a highly strained transition state [18], consequently improving the catalytic properties of the material.

Summarizing, it was demonstrated on the nano-scale how small organic modifications to the zeolite framework can have a considerable effect on the fundamental catalytic properties and reactivity of the hybrid organic/inorganic material. However, neither methylene nor amine groups can be located on the aluminum tetrahedron without being automatically protonated, which in

the case of methylene-modified zeolites even results in cleavage of the ordered framework.

## Conclusions

The candidate's thesis shows very clearly how theoretical modeling is capable of providing new insights into zeolite catalysis. Moreover, the art of molecular modeling has evolved from merely reproducing experimental data to solving high-profile conundrums for which no clear-cut experimental solutions are available. The highly-debated controversy regarding the direct mechanisms in the MTO process has been ended once and for all and new insights into the alternative hydrocarbon pool proposal have revealed unexpected features of the supramolecular behavior of a combined homogeneous/heterogeneous catalyst. Furthermore, a first step towards catalyst optimization has been made by studying the effect of small organic moieties on the catalytic behavior of brand-new zeozyme materials. The issue of framework cleavage for methylene-modified zeolites has been solved and amine functionalizations have been shown to radically improve catalytic properties. The rapid evolution in this field of research, even within the time-scale of this thesis, makes it as good as certain that further significant advances will soon be within reach.

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