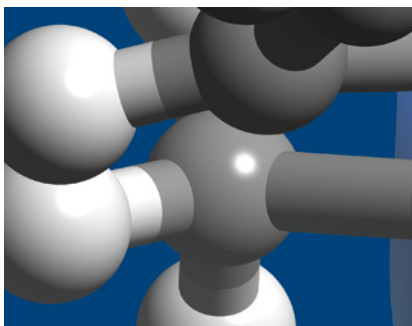


COMPUTATIONAL STUDIES OF THE METHANOL TO GASOLINE PROCESS – IMPROVED CATALYSTS AND PROCESSES



The study demonstrates that DFT is a powerful tool for studying zeolite-catalyzed reactions. The method provides quantitative predictions about thermochemistry and energy barriers, and in addition provides insight at the molecular level, which can be used in the development of new catalysts.

Module used

- Materials Studio — DMol³

Industry sectors

- Catalysis
- Petrochemicals

Researchers at Accelrys have used the Density Functional Theory (DFT) code DMol3, available in Materials Studio®, to study important reaction mechanisms in the conversion of methanol to gasoline (MTG).¹ The study determined the reaction pathways and energy barriers to the activation of the C-O bond of methanol and the formation of the first C-C bond in the hydrocarbon chain. The work discovered new, lower energy mechanisms, and demonstrates the importance of using realistic models when simulating these types of processes. The results contribute to a molecular-level understanding of MTG reactions, and can be used to develop improved catalysts and processes.

INTRODUCTION

The conversion of methanol to gasoline (MTG) has become particularly important in recent years as consumers seek alternatives to fossil fuels. A thorough understanding of the reactions involved in MTG is, of course, essential to developing efficient MTG processes. Despite much industrial and academic research, details of the mechanism remain unresolved. The reaction is initiated by dissociating the C-O bond of methanol. The species formed react initially to form compounds such as dimethyl ether or ethanol. Of

particular interest is the mechanism for forming the initial C-C bond in these molecules. A number of mechanisms have been proposed,² including a mechanism involving a surface ylide.^{3,4}

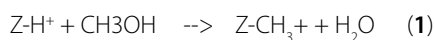
In this work, scientists at Accelrys investigated the mechanisms of these reactions using periodic DFT calculations. The results include a new low-energy path to formation of ethanol. Although a stable ylide intermediate was discovered, it involved a higher energy barrier.

RESULTS

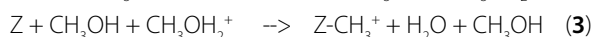
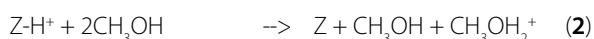
DFT calculations were performed using Accelrys' DMol³ DFT program. First principles calculations on zeolites have often involved cluster models to approximate the neighborhood of the Brønsted acid sites.^{2,5} Such models, however, generally do not contain all the acid sites in a single cavity, and make it difficult to relax the zeolite framework in a consistent manner.

Experimentally, the MTG reactions take place in large zeolites such as ZSM-5. This is prohibitively large for performing DFT calculations, so in this work the authors used FER zeolite, which contains 8-rings and 10-rings of comparable size. Prior to modeling the entire reaction pathway, the choice of smaller zeolite was validated by computing the binding energy of methanol in both frameworks.

The initial reaction of methanol in an activated zeolite (Z) may be written as:



The computed barrier was 54 kcal/mol. Introducing a second methanol into the zeolite cavity, as shown in Fig. 1, results in a reaction in which one molecule acts as a spectator in the formation of a methoxonium ion:



The methoxonium ion, CH_3OH_2^+ in reaction (2) forms spontaneously. The computed energy barrier to cleaving its C-O bond (reaction 3) is only 44 kcal/mol, significantly lower in energy than the corresponding process without the second methanol present.

The surface-bonded methyl group can react with methanol to form dimethyl ether or ethanol, which are the first species to contain a C-C bond.

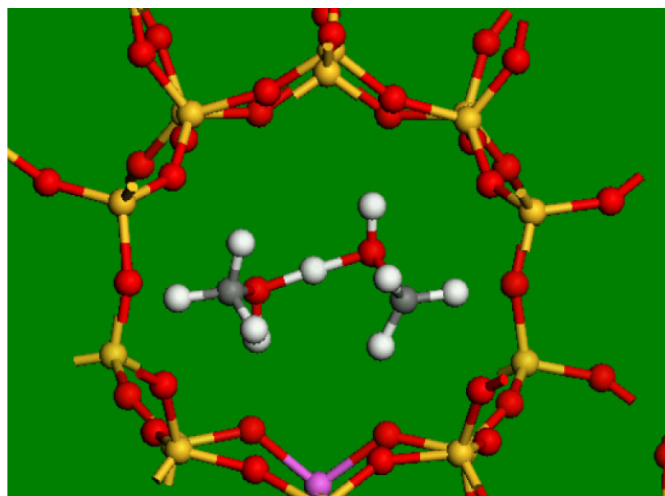
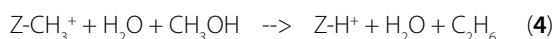


Fig. 1 Transition state structure for reaction (3), the formation of CH_3^+ and H_2O from methanol and methoxonium ion.

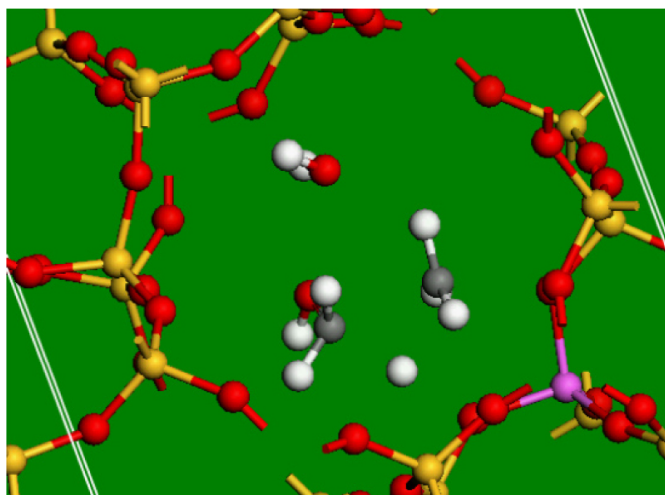


Fig. 2 Transition state structure for reaction (4), the formation of ethanol.

The formation of ethanol is shown in Fig 2. This reaction has a barrier of 50 kcal/mol and is exothermic by 22 kcal/mol. This was the first identification of this pathway, which is energetically competitive with ones previously reported.^{4,6}

CONCLUSIONS

This work elucidated key reaction mechanisms involved in the breaking of the C-O bond and the formation of the first C-C bond in the MTG process. Periodic DFT calculations are necessary to account for the significant reorganization of the zeolite cage that occurs. The work identified a new route for ethanol formation, indicating that competing reaction pathways are probably present. The study demonstrates that DFT is a powerful tool for studying zeolite-catalyzed reactions. The method provides quantitative predictions about thermochemistry and energy barriers, and in addition provides insight at the molecular level, which can be used in the development of new catalysts.

To learn more about Materials Studio by Accelrys, go to accelrys.com/materials-studio

REFERENCES

1. N. Govind, J.W. Andzelm, K. Reindel, G. Fitzgerald, *Int. J. Mol. Sci.* **2002**, 3, 423.
2. G.J. Hutchings and R. Hunter, *Catal. Today*, **1990**, 6, 279.
3. G.J. Hutchings, G.W. Watson, and D.J. Willock, *Micro. Meso. Mat.*, **1999**, 29, 67.
4. S.R. Blazzkowski and R.A. van Santen, *J. Am. Chem. Soc.*, **1997**, 119, 5020.
5. P.E. Sinclair and C.R.A. Catlow, *J. Chem. Soc. Faraday Trans.*, **1996**, 92, 2099.
6. J. Andzelm, N. Govind, G. Fitzgerald, A. Maiti, *Int. J. Quantum Chem.*, **2003**, 91, 467.