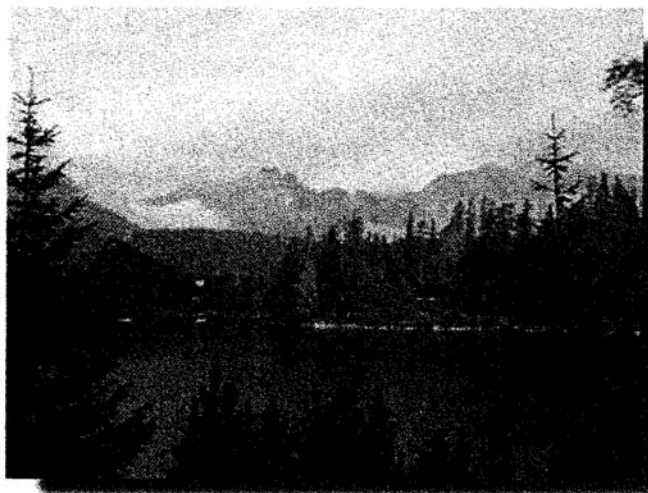# 9th Pannonian International Symposium On Catalysis

8 – 12 September 2008

Štrbské pleso
High Tatras National Park
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A COMPUTATIONAL STUDY ON THE ADSORPTION OF THE MAJOR RING-TRANSFORMATION PRODUCTS OF METHYLOXIRANE IN HY AND HZSM-5 ZEOLITES

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Abstract

The adsorption of dioxolane and dioxane derivatives in HY and HZSM-5 zeolites was studied computationally. The molecules are the main ring-transformation products of methyloxirane over these zeolites. Experimental work showed that the cyclic dimerisation reaction starts with the adsorption of the monomers over Brønsted acid sites through their ring oxygens. Computations revealed that these sites were close enough even in the high-silica HZSM-5 zeolite and the dimers comfortably fit even in the β-cage of HY as well as in the channel of the HZSM-5 zeolites. The stereochemical outcome of the dimerisation was also studied and the optimum conformations of the dimers were calculated as well.

Keywords: ring-transformation reactions; methyloxirane; HY; HZSM-5; computations.

Introduction

Epoxides are extremely useful building blocks in the synthesis of various complex organic molecules and macromolecules [1]. There versatility lies in the fact that they can be easily prepared, under normal circumstances (room temperature, atmospheric pressure) they are stable yet the rings are reactive enough: they can be opened in stoichiometric as well as in homogeneous or heterogeneous catalytic reactions. The catalysts can be solids of various types, among others acidic molecular sieves [2]. Part of the versatility is the ability of these compounds to transform in various ways especially if the rings are substituted.

During our earlier investigations concerning the ring-opening reactions of methyloxirane over aluminosilicates of various types [3] it was found that single as well as double C-O scission occurred producing oxo compounds and olefins. It also became clear that the major reaction pathway was cyclic dimerisation producing various dioxolane and dioxane derivatives (Scheme 1).

It was observed that on H-form zeolites (actually, the deuterated forms were used) Brønsted acid site pairs could be the reaction centres [4] (Scheme 2), however, the possible locations where the dimerisation reactions proceed could not be unfolded nor the optimum conformations of the dimers could be described. These problems can be targeted through molecular modelling, by choosing large enough models to resemble the actual zeolite used in the experimental work and studying the behaviour of the reactant and the product molecules in these models computationally. Results of such a work are described in this contribution.

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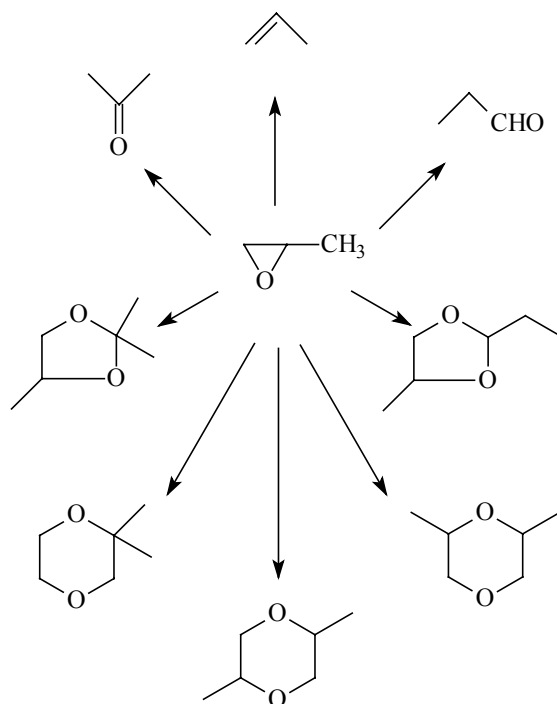
Scheme 1. Transformation pathways of methyloxirane over acidic zeolites
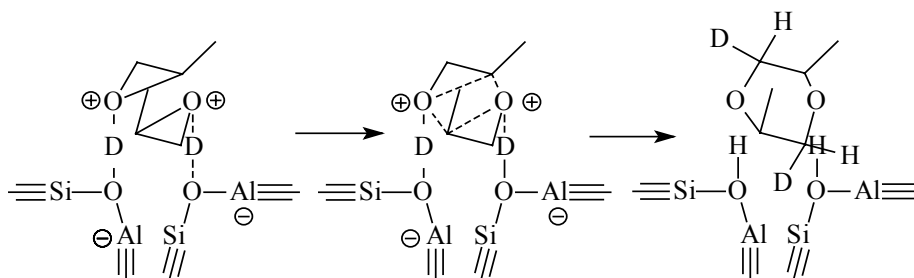
Scheme 2. A possible route for the formation of a d_2-dioxane derivative over a pair of Brønsted acid centres.

Method of computations

The pdb files of the Y and the ZSM-5 zeolite crystals were obtained from databases and were transformed manually to resemble the experimentally used samples the best. Portions of crystal structures were cut to bear all features of the actual zeolite and the dangling oxygen bonds were closed with hydrogen atoms. The Si/Al ratios in the sample were set to be close to those of the experimentally used molecular sieves (14 and 2.5 for HZSM-5 and HY, respectively).

Two methyloxirane molecules were bonded to Brønsted sites as close to each other as it was possible in locations characteristic for the actual zeolite. The possible product dimers made from the monomers were also bonded to the same active sites.

The reactants and also the dimers were optimised together with the appropriate portion of the zeolite with the PM3 semiempirical code [5] included in the Hyperchem package [6]. Full geometry optimisation was performed with gradient norm of 0.1. The obtained stationary points were checked to be minima.

The model crystals were so large that methods of higher theoretical level could not be applied.

Results and discussion

Methyloxirane and the cyclic dimers in the HZSM-5 model
Two views of the applied crystal model for the HZSM-5 are seen in Figure 1.
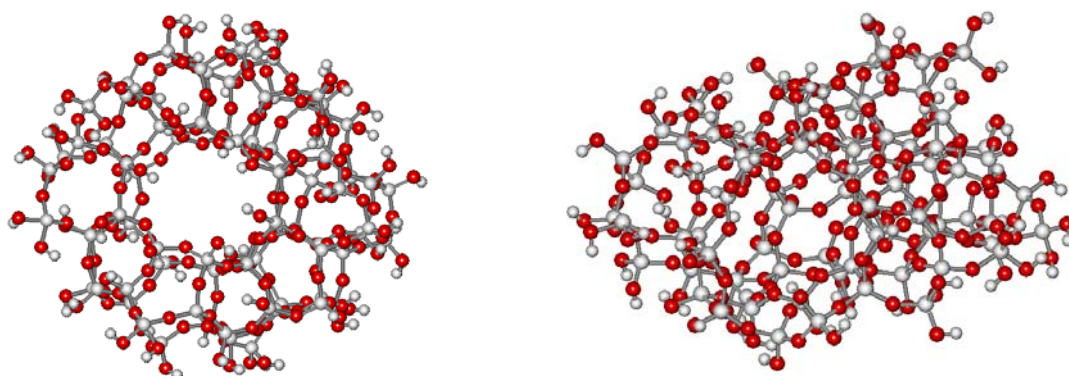
(a)   (b)
Fig.1. Two HZSM-5 models applied in this study, (a) top view, (b) side view.

This model served for the accommodation of two methyloxirane molecules. They were placed in the vicinity of the Brønsted acid sites pointing towards the interior of the larger (straight) channel.
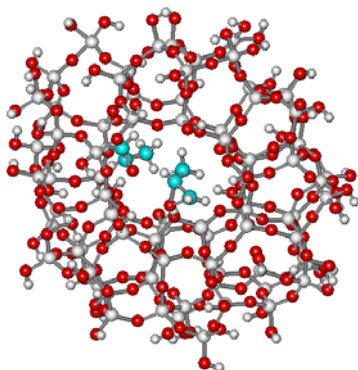

Fig.2. Two methyloxirane molecules in close proximity in the straight channel of HZSM-5.

Those sites were searched and found, which allowed the two molecules to be in relatively close proximity. Optimisation revealed that the molecules stayed in the channel and close to each other (Figure 2).

It was not surprising that both the dioxolane and the dioxane derivatives either in the *cis* or *trans* configuration were also comfortably placed in the channel (Figure 3). Obviously, they can diffuse through the channel easily, in complete accordance with the observation that cyclic dimerisation was the main pathway of ring transformation.

Methyloxirane and the cyclic dimers in the HY models
The HY zeolite has a more complex structure than HZSM-5. Its supercage and the 'windows' leading to it (Figure 4a) are large enough for the accommodation and easy transportation of two methyloxirane molecules as well as the cyclic dimers. However, the sodalite unit with its hexagonal prisms (Figure 4b) are much smaller and it is not trivial that two methyloxirane molecules and the dimers find enough room for adsorption and the movement of the dimers may also be considerably hindered.
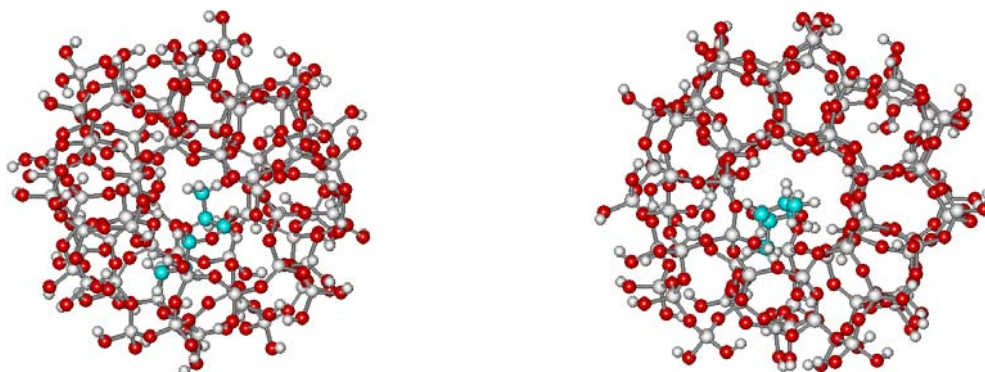
(a)   (b)

Fig. 3. Cyclic dimers in the straight channel of HZSM-5, (a) *trans*-2-etil,-4-metil-1,3-dioxolane, (b) *cis*-2,5-dimetil-1,4-dioxane.
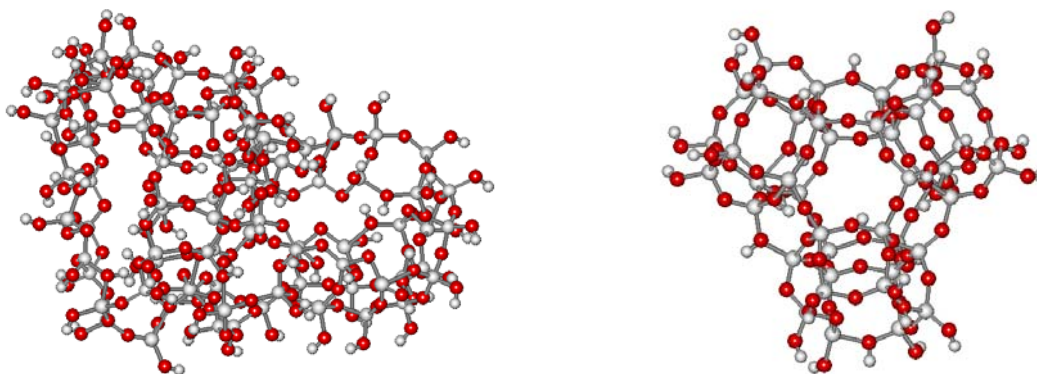
 (a)   (b)

Fig. 4. Structural models of the HY zeolite, (a) two supercages, (b) sodalite unit plus the hexagonal prisms.

Indeed, the two methyloxirane molecules (Figure 5a) could be comfortable placed at each other's vicinity and there was no steric hindrance for cyclic dimerisation to occur either (Figure 5b, only the dioxolane derivative is shown).
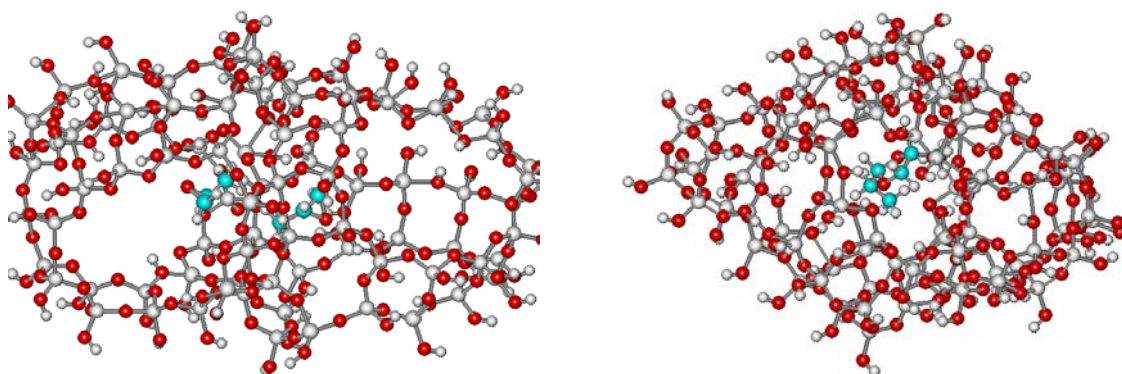
(a)   (b)

Fig. 5. The two methyloxirane molecules (a) and the dioxolane dimer (*cis*-2-etil,-4-metil-1,3-dioxolane) in the supercage model of HY.
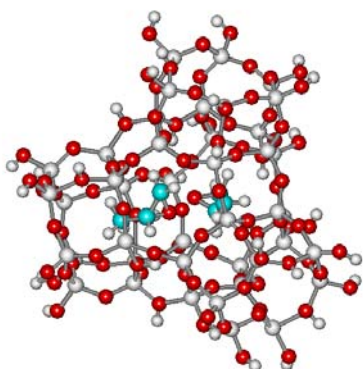
Fig. 6. The two methyloxirane molecules in the smaller (sodalite cage plus hexagonal prisms) structural model of HY
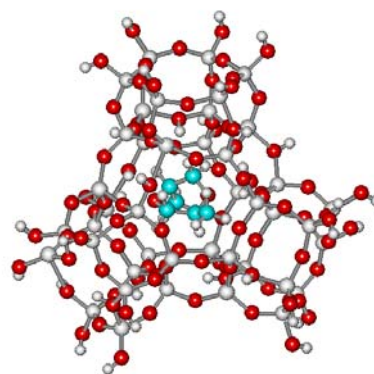
Molecular modelling may give clue whether the smaller structural unit (sodalite cage plus the hexagonal prisms) can participate actively in the cyclic dimerisation or not.

It was revealed that the two methyloxirane molecules fitted to the inner space of the model and they could be placed close enough to each other to facilitate easy dimerisation. Diffusion of the dimers through these pores is certainly more difficult than into or out of the supercage, nevertheless, dimers could be comfortably accommodated (Figure 7) and most probably this part of the zeolite was also active in this ring-transformation reaction.
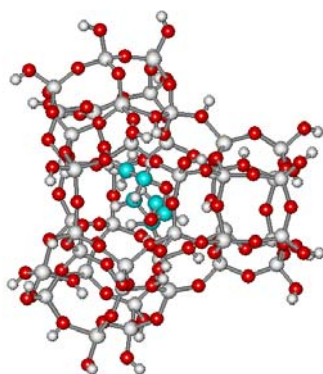
(a)   (b)

Fig. 7. Cyclic dimers in the smaller HY model (sodalite unit plus hexagonal prisms), (a) *cis*-2-etil,-4-metil-1,3-dioxolane, (b) *trans*-2,5-dimetil-1,4-dioxane.

This type of molecular modelling does not tell us whether the reaction actually takes pace or not, let alone giving information about the elementary events occurring during reaction. Nevertheless, having the experimental knowledge that these types of transformations actually do take place, one may obtain a pictorial view about steric possibilities of adsorption, dimerisation and transportation of the reactants as well as the cyclic products. One may also be able to judge whether certain parts of the catalysts are actively catalyse the reactions or they are merely bottlenecks.

It turned out that both the experimentally observed most abundant dioxolane and dioxane stereoisomer derivatives could be accommodated in every characteristic locations of the zeolites and the molecular traffic was largely unhindered. The most probable conformations of the dimers could also be determined.

Conclusion

This work verified that molecular modelling nicely complements experimental work and helps in obtaining a more complete description of the chemical events at the molecular level.

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