Computer simulation studies of the selectivity of zeolites for different butene isomers

Petra Tomlinson-Tschaufeser[a] and Clive M. Freeman[b]

[a] *Institut für Mineralogie und Petrographie, Universität Innsbruck, Innrain 52, 6020 Innsbruck, Austria*
[b] *Molecular Simulations Inc., 9685 Scranton Road, San Diego, CA 92121, USA*

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In the present study simulation methods are applied to investigate butene isomer selectivity in 55 zeolite structures, and to rank the predicted performance of potential zeolite catalysts. The method used is based on a blend of Monte Carlo and molecular dynamics with energy minimization procedures. The TON framework has the highest ‘selectivity’ followed by RHO and MFI. The calculations indicate that the TON (Theta-1) framework is particularly effective in binding differing butene isomers in differing manners.

Keywords: zeolites, computer simulation, Monte Carlo docking, sorption, butene isomers

1. Introduction

The selectivities of microporous isomerization catalyst materials depend on a complex blend of factors. The relative thermodynamic stabilities of product isomers is of importance, though often free energies of formation for important isomers are similar. Also relevant are the relative diffusivities of isomers through the catalyst matrix and the presence of pore modifying species within the matrix. The crystalline regularity of microporous materials, however, also provides a means by which the catalyst material interacts in a highly specific manner with the products of the reaction that it catalyzes. Although such interactions are unlikely to be the sole determinant of catalyst behavior, the magnitude and range of such effects is of interest. Modelling methods provide valuable insight into the mechanism of shape selectivity through the simulation of intermolecular interactions between guest molecules and porous host materials.

In this work the selectivity of different zeolites for the four isomers of isobutene is studied (figure 1). This system has been chosen for study because it is commercially and environmentally important. But-1-ene is produced in large quantities in the petrochemical industry as a by-product of catalytic cracking. The manufacture of isobutene using acid catalysts is desirable as this material, upon reaction with methanol, yields methyl *tertiary*-butyl ether (MTBE), an important fuel additive [1].

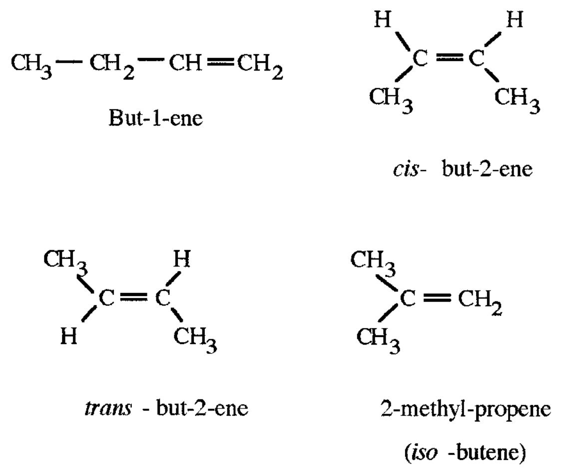
MTBE is already produced in large quantities, with significant economic value, providing considerable incentive for the improved understanding of precursor production.

In this paper we report an investigation of the comparative sorption of butene isomers within a range of zeolite structures. The addition of ZSM-5 to cracking catalysts is known to increase the iso/normal ratio for olefins [2]. An earlier study [3] has targeted butene sorption in the single host structure silicalite. Simulation methods were used to probe the selectivity of butene isomers by one zeolite, zeolite ZSM-5, thereby demonstrating that the type of modelling approach that will be applied in this work can indeed be used to investigate catalyst selectivity. Similar techniques have been employed in understanding the interaction of structure directing agents with microporous hosts [4–7].

In the present study computational methods are applied to investigate butene isomer selectivity in 55 zeolite structures, and to rank the predicted performance of potential zeolite catalysts.

2. Methodology

The methodology of the present study is summarized in figure 2. The process begins with a high-temperature molecular dynamics trajectory calculation for the sorbate


But-1-ene

cis- but-2-ene

trans - but-2-ene

2-methyl-propene (*iso* -butene)

Figure 1. The four isomers of isobutene.

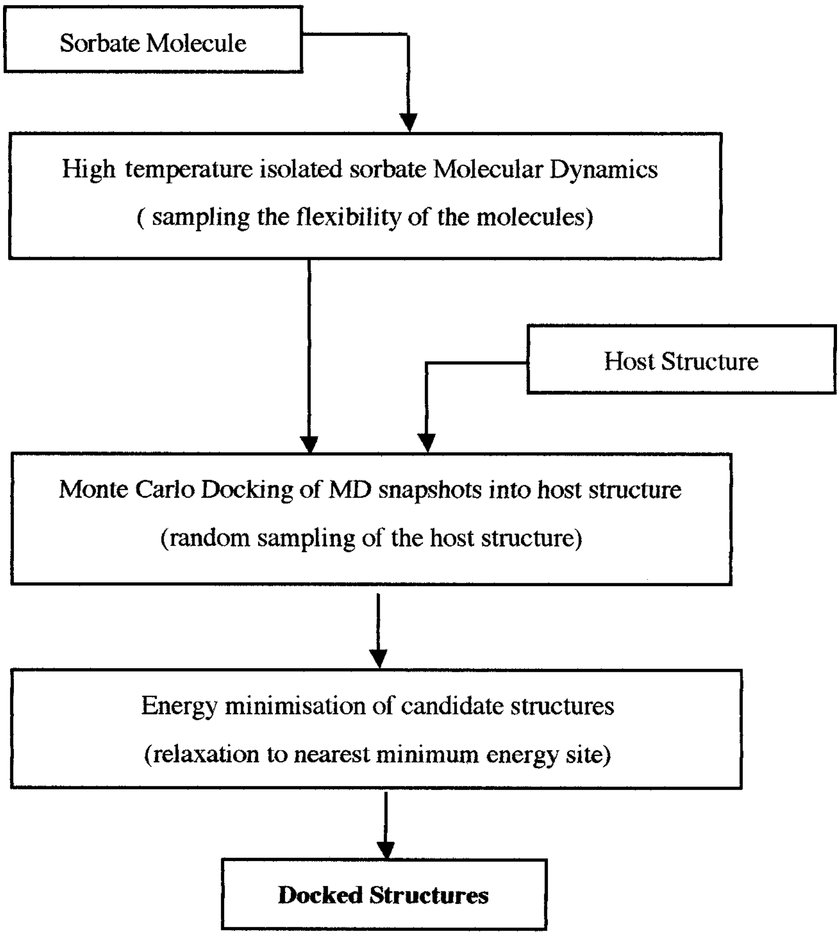


Figure 2. Summary of the docking method.

molecule in vacuum conditions. This molecular dynamics trajectory will sample a range of the conformational possibilities of the sorbate molecule. The butene isomers are comparatively inflexible, possessing only rotatable methyl groups and, in the case of but-1-ene a carbon–carbon torsion. However, the molecular dynamics sampling of sorbate configurations allows for the possibility of binding stabilizing structures which are unfavorable in the gas phase. (For simple model systems such as biphenyl, for example [8], the packing of the crystal structures promotes a structure which deviates significantly from the gas-phase equilibrium configuration.) These structures are used as candidates for Monte Carlo docking within the host framework. The subsequent docking procedure is based on the random (i.e., Monte Carlo) selection of positions and molecular orientations within the host followed by calculation of a trial interaction energy for the host–guest molecule system. A trial structure is accepted if its energy is lower than a defined threshold. The calculation is performed on structures with periodic boundary conditions. This Monte Carlo procedure leads to the generation of one docked structure for each conformation saved in the molecular dynamics trajectory of the isolated guest molecule. It should be noted that the Monte Carlo procedure applied in this study differs from the well known importance sampling technique of Metropolis et al. [9], where the structure depends on the previously accepted conformation. In the present procedure successive conformations are generated at random throughout the host structure.

Once docked, each combined structure is then allowed to relax to an energy minimum structure.

Energy minimization and molecular dynamics calculations employed DISCOVER [10]. The potential parameters were taken from the consistent valence force fields (CVFF) [10]. The parameters are available from the authors. As in previous studies, molecular dynamics calculations of the guest molecule were performed at a temperature of 1500 K in order to generate multiple conformers of the four butene isomers. The zeolite structures used are taken from the compendium of Insight II version 400 library [11]. Calculations were performed with purely siliceous zeolite structures. Periodic boundary conditions were used to simulate the infinite nature (effectively infinite when viewed from a microscopic perspective) of the zeolite.

3. Results

The sorption energies, as defined above, of each butene isomer were calculated for 100 different configurations for each host structure and from these energies the average

Table 1
The average binding energy and selectivity of the butene isomers in zeolites.

Zeolite	Type of access		Average binding energies (kcal/mol)				Selectivity
			Isobutene	But-1-ene	*Trans*-but-2-ene	*Cis*-but-2-ene	but-1-ene/isobutene
LEV	8,8	2D	−11.74	−13.74	−12.04	−11.19	1.17
MTW	12	1D	−13.43	−15.71	−14.60	−13.11	1.17
HEU	8,1	2D	−12.65	−14.57	−12.35	−12.04	1.15
EUO	10	1D	−12.14	−13.92	−12.54	−11.50	1.15
MTT	10	1D	−13.09	−14.79	−12.49	−12.69	1.13
PHI	8,8,8	3D	−11.27	−11.92	−9.01	−7.18	1.06
BRE	8,8	2D	−13.01	−13.25	−4.99	−11.58	1.02
ERI	8,8,8	3D	−10.47	−10.64	−10.95	−10.15	1.02
MAZ	8,8,12	3D	−9.61	−9.73	−8.73	−8.20	1.01
LOS	6-rings	0D	−13.75	−13.84	−13.05	−11.75	1.01
SOD	6-rings	0D	−11.84	−11.80	10.87	−6.23	1.00
THO	8,8,8	3D	31.75	29.14	38.36	37.72	0.92
NON	6-rings	0D	−14.79	−12.97	−12.65	−14.22	0.88
FAU	12,12,12	3D	−3.34	−2.91	−3.78	−2.79	0.87
ANA	8-rings	0D	122.52	104.23	86.92	112.91	0.85
NAT	8,8,8	3D	72.36	60.73	54.62	68.97	0.84
YUG	8,8	2D	4.27	2.97	3.48	5.56	0.70
BIK	8	1D	75.49	46.51	32.72	41.76	0.62
GOO	8,8,8	3D	−12.41	−7.18	−1.08	−4.46	0.58
ABW	8	1D	86.01	43.15	27.80	48.37	0.50
MEP	6-rings	0D	−11.38	−3.79	0.00	−9.32	0.33
MON	8,8,8	3D	21.64	6.25	4.16	10.38	0.29
JBW	8	1D	38.99	5.10	0.13	12.67	0.13
EDI	8,8,8	3D	−0.84	3.85	8.32	11.36	−4.58
DOH	6-rings	0D	−6.03	−13.59	−11.31	−9.89	2.25
AFG	6-rings	0D	−4.80	−10.71	−4.47	−8.63	2.23
TON	**10**	**1D**	**−9.88**	**−18.57**	**−18.49**	**−14.07**	**1.88**
RHO	8,8,8	3D	−5.00	−8.75	−7.38	−5.31	1.75
MFI	10,10,10	3D	−5.07	−8.27	−6.68	−5.00	1.63
MOR	8,12	2D	−4.83	−7.60	−5.97	−3.34	1.57
EMT	12,12,12	3D	−3.50	−5.43	−4.05	−3.18	1.55
LTL	12	1D	−5.44	−8.09	−5.23	−4.87	1.49
MTN	6-rings	0D	−10.86	−15.64	−11.53	−11.37	1.44
DAC	8,1	2D	−10.74	−14.66	−12.90	−8.94	1.36
MEI	7,12	2D	−6.71	−9.03	−7.21	−6.07	1.35
BOG	10,12	3D	−7.61	−10.19	−9.02	−7.53	1.34
FER	8,1	2D	−6.47	−8.65	−7.56	−6.10	1.34
MER	8,8,8	3D	−8.63	−11.49	−8.95	−6.09	1.33
LIO	6-rings	0D	−6.95	−9.07	−15.13	−4.69	1.30
GME	8,12	2D	−7.91	−10.17	−8.42	−7.50	1.29
MFS	8,1	2D	−11.06	−14.17	−13.59	−11.82	1.28
MEL	10,10,10	3D	−10.99	−14.05	−12.91	−11.48	1.28
GIS	8,8,8	3D	−6.62	−8.27	−7.49	−3.05	1.25
DDR	8,8	2D	−10.09	−12.57	−11.19	−11.08	1.25
EPI	8,1	2D	−10.59	−13.12	−11.48	−8.89	1.24
LTA	8,8,8	3D	−5.03	−6.21	−6.26	−5.09	1.23
OFF	8,8,12	3D	−9.73	−11.86	−9.85	−9.29	1.22
CAN	12	1D	−5.66	−6.86	−6.82	−7.02	1.21
KFI	8,8,8	3D	−8.08	−9.76	−8.21	−7.42	1.21
CHA	8,8,8	3D	−9.94	−11.99	−10.42	−9.31	1.21
NES	10,1	2D	−11.07	−13.33	−11.71	−10.58	1.20
LAU	10	1D	−13.61	−16.33	−14.94	−13.21	1.20
SGT	6-rings	0D	−12.98	−15.37	−13.62	−12.96	1.18
EAB	8,8	2D	−11.37	−13.44	−11.34	−11.05	1.18
STI	8,1	2D	−12.01	−14.12	−11.74	−11.56	1.18

sorption energy was evaluated. The unweighted average energies over the complete set of minima obtained are listed in table 1. Also tabulated are the type of access for each zeolite type indicating accessibility to the butene isomers. Structures with no overall channel system (structures with only 6-ring pores) were included in the calculation to ac-

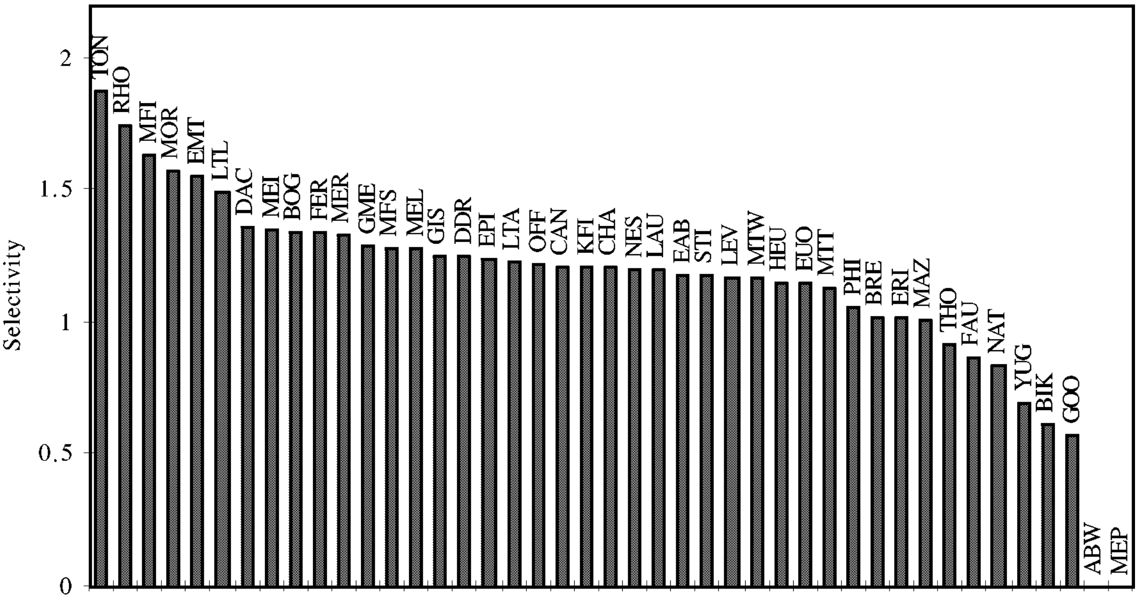


Figure 3. Selectivity of butene isomers (selectivity: but-1-ene/isobutene); zeolites with no channel system are not considered in this graph. The zeolites are sorted according to their selectivity.

cumulate knowledge of the structural features which maximize butene selectivity in novel materials [12].

The computed binding energies of table 1 show the substantial effect that differing hosts have on the relative binding energetics of the butene isomers. The ratio of but-1-ene to isobutene binding energies, termed ‘selectivity’ here, and tabulated in table 1, highlights the differing binding characteristics of the zeolite host structures studied. The variation of this measure of the comparative binding of but-1-ene and isobutene for the range of framework types investigated is shown graphically in figure 3.

4. Discussion

The binding energies of the calculations reveal the degree to which the hydrocarbon molecules are able to optimize their interactions with the zeolite host structure. The binding energy is most favorable where the number of favorable interactions is maximized without imposing internal strain on the hydrocarbon. Thus the smaller pore zeolite materials (with ring dimensions of 8 and 10) have larger binding energies than structures with 12-rings. For a number of structures which possess only 8-rings (such as YUG and THO) the resulting channel structure is too small to accommodate the isomers and hence unfavorable positive binding energies are obtained.

The relative difference in degree of binding for isobutene and but-1-ene varies with the differing zeolite framework types (figure 3, table 1). The range of relative binding energies is large. The ratio of binding energies but-1-ene : isobutene is 0.5–1.8. In TON isobutene has almost half the binding energy of but-1-ene, whereas in MAZ both isomers bind with approximately equal strength.

Those materials that exhibit the largest calculated binding energy differences show the largest difference in the binding mode for the differing isomers. In the case of TON, for example, the comparatively linear but-1-ene molecule is frequently determined to be able to occupy low-energy sites with a large number of favorable interactions with the framework, spanning the channel. In contrast, the isobutene molecule in TON is not able to span the pore structure to obtain a similar number of favorable interactions. In FAU, for example, there are comparatively small differences in the binding of but-1-ene and isobutene and this is reflected in a small calculated binding energy difference.

The characteristic that promotes high selectivity, then, is an internal pore geometry which provides good registry with the dimension of one adsorbate in comparison with another adsorbate. For TON this is obtained by the cross-channel mode of binding accessible to only the but-1-ene isomer. For FAU no pore features are present in the range of dimensions exhibited by the butene isomers and low degrees of selectivity are obtained in the calculations. The broad range of structures considered permits the examination of zeolites in which differences in isomer binding energies are most pronounced. The simulation studies have shown that the TON framework has the highest selectivity compared to other frameworks evaluated.

This study demonstrates that differing framework types are able to interact with reaction products in differing manners even when these products have dimensions smaller than those typically associated with shape-selective effects. This study also shows how computer simulation can provide information about the origin and magnitude of such effects.

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