## Shape selectivity in zeolites

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## Shape Selectivity in Zeolites

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Cover: Photo showing a manhole cover in front of the conference hall at the 13th International Zeolite Conference, Montpellier, France (2001).

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## **I** Introduction

In many cases a chemical reaction may produce a lot of different products, of which only a few are wanted, or even just one. So rather than isolating the desired products from the final reaction mixture, it is preferable to control the selectivity of a reaction in such a way that only the desired products are formed. Not only will this save a lot of effort, but it also saves additional chemicals, materials, and energy, resulting in more sustainable processes.

A well-known example is the synthesis of pharmaceutical products. For a molecule to be biologically active, it needs to be of the correct chiral form, i.e. it has to have not only the correct connectivity between the atoms, but also the correct threedimensional arrangement. This is because living organisms have a tremendous ability to perform chemical reactions with high selectivity. As a result, pharmaceuticals have to be of precisely the right shape to be able to interact in the manner intended. Many catalysts with the ability to perform reactions at very specific sites of a molecule with high selectivity have been developed in the past decades.

At night, driving past beautifully illuminated oil-refineries with their big installations towering high above the freeway, it might perhaps not be so obvious that the need for control over the selectivity of a chemical reaction is not limited to the field of fine chemicals but also very much present in the field of bulk petrochemistry. For small hydrocarbons, like methane and ethane, there is only one isomer, but for larger hydrocarbons the number of isomers increases exponentially: from 2 in the case of  $C_4$ to 355 in the case of  $C_{12}$ . Not all of these isomers are equally valuable, thus creating a need for the selective conversion of isomers into more valuable ones. For example, in the production of gasoline it is necessary to increase the octane number of the light naphtha fraction, produced by distillation of crude oil, by selectively converting linear alkanes into double branched alkanes. The processes involved, although around since the 60's and 70's, have recently regained attention as environmental legislation in western nations demand the total removal of additives like MTBA and lead, thus increasing the need for highly selective catalysts [1]. A slightly different selectivity is required during treatment of the heavier fractions from the distillation process to produce high-quality lubricant oil. To prevent the oil from forming a sludge at low temperatures one also wants to introduce selective branching of the hydrocarbon backbone, but this time only at a moderate level. This requires a different performance of the catalyst compared to that of the gasoline example where the highest possible degree of branching is preferred. The catalysts used in the petrochemical industries

to perform these selective hydrocarbon conversions are often based on zeolites [1].

Zeolites are microporous crystalline materials, build up from TO<sub>4</sub> tetrahedral units, were the central T atom is usually Silicon or Aluminium. The units are linked through the oxygen atoms, creating three-dimensional networks which define voids within them. These voids may have cylindrical pore or cage-like morphology and additionally, depending on the type of zeolite structure, the pores and cages are linked in a one-, two-, or three-dimensional way. The pores are often big enough to allow small molecules, like alkanes or water, to enter. There are now over 130 known zeolite topologies, of which several can be found in nature [2]. Any zeolite structure, irrespective of its chemical composition, is categorized by a three letter code. In other words, the chemical properties of zeolites can be altered without changing the basic topology of the pore system. A common alteration to chemical composition is a change in the Si to Al ratio. All silica zeolites are chargeless. A net charge can be created by substituting a Si atom by an Al atom. This will create a negative charge on the Al tetrahedron, which has to be balanced by a counter ion or a proton. In the latter case a hydroxyl-group with strong Brønsted acid properties is created, which can be used in hydrocarbon chemistry [3]. An example of a typical zeolite framework is given in Figure 1.1 in the form of the all silica version of the MFI topology, Silicalite-1. The three-dimensional pore system of MFI comprises intersecting straight and zig-zag channels, both approximately 5.5 Å in diameter.

Because of their special structure and stability, zeolites are used in many applications. These include, besides the petrochemical ones already discussed, fertilizers, pigments in paint, nanoscale lasers, medical applications, and self-cooling beer kegs [4–8]. The largest application in terms of volume is the use of zeolites as ionexchanger in detergents.

In this study we try to understand the intrinsic differences in adsorption and catalytic behavior between various topologies in hydrocarbon processing. The approach will be to link the shape selectivity observed in these processes to adsorption thermodynamics. Computer simulations are used to obtain the necessary thermodynamic data needed for such an assessment by calculating the adsorption behavior of different alkanes isomers at both low (chapter 4) and high alkane loading (chapters 3 and 5) inside the zeolitic pores. In this way detailed information on a molecular level about the adsorbed alkanes is obtained, i.e. how well do they fit inside these confined environments. This kind of information enables us to explain experimentally observed differences in selectivity between different types of zeolites and make predictions about the optimal zeolite-based adsorber or catalyst plus corresponding operating conditions for a particular process.

### 1.1 The use of zeolites in oil refining

The refining of crude oil is a major industry which makes heavy use of zeolites in many parts of the refining process [1]. Crude oil is first split, according to boiling point, in various fractions in a primary distillation step. Each fraction is subsequently fine-tuned to the desired application by further purification and upgrading. Zeolites



**Figure 1.1:** The structure of the zeolite Silicalite-1 (MFI topology) projected on the ac-plane (left) and the bc-plane (right). The oxygen atoms are dark grey, the silicon atoms light grey. The straight channels run along the b axes (left), the zig-zag channels run in the ac-plane (right). Both channels have a diameter of approximately 5.5 Å.

come in to play in many of these upgrade processes [1], a selection of which is outlined below:

• The naphtha fraction with boiling range up to 180°C, destined to become transportation fuel, is treated to increase the octane number by the selective hydroconversion of linear alkanes into branched isomers. This is usually a two stage iterative process which combines a separation process, to split the naphtha into a linear alkane fraction and branched alkane fraction, with a catalytic step to introduce branching in the linear fraction. The separation process is usually based on molecular sieving with the use of small pore zeolites like LTA. The linear alkane fraction is subsequently fed to a hydroisomerization reactor based on medium-to-large-pore acid zeolites loaded with noble metals, like Pt-H-MOR, for conversion. The output of this reactor is then fed back to the separation process.

Another way of increasing the octane number of the gasoline is to selectively crack the linear alkanes to light gaseous alkanes. Catalysts based on medium pore zeolites, like MFI or FER, are particularly suited to perform these selective cracking reactions.

- The middle distillates are used to produce heavier fuel types like kerosene (boiling range 130° to 300°C) and diesel/gas oil (boiling range 150° to 370°C). For these fuels a high hydrogen content is desired. Catalysts based on noble metal loaded acid zeolites are used in the hydrogenation process to produce alkanes fully saturated with hydrogen. Additionally the gas oil fraction can undergo a de-waxing step, similar to the lubricant de-waxing explained below. This enables the use of the gas oil in low temperature environments, and allows for the addition of more heavy fractions to the alkane mix.
- The fraction with a boiling range around 370°C also contain base oils used in the production of lubricants. These oils consist for a large part of long normal alkanes, and are therefor prone to sludge formation at low temperatures. The easy alignment of the normal alkanes can be broken by the selective hydroisomerization of some of the normal alkanes into lightly branched isomers. Medium pore zeolites, and especially those with small 10-ring uni-directional pores, have proven to be highly selective de-waxing catalysts.
- The fractions with a boiling range higher than 370°C, like the vacuum gas oil and the residue, are not very useful without severe processing. They are converted into usable lighter alkanes by catalytic cracking over acid catalysts based on FAU. This process accounts for more than 90% of the zeolites produced for catalytic applications.

The above-mentioned examples where selected on the basis of relevance to this thesis and cover by no means all applications of zeolites in the refining and petrochemical industries.

### 1.2 Acid catalysed hydrocarbon hydroconversion

Before addressing the effect of zeolite induced shape selectivity on the hydroconversion reactions, it is worthwhile to first discuss what occurs in the absence of shape selectivity.

In alkane hydroconversion, a metal site dehydrogenates alkanes into an alkene, an acid site converts the alkene into another isomer or a cracking product, whereupon the metal site hydrogenates the converted alkene back into an alkane [9–11]. When starting with an n-alkane, the hydroconversion can be described as a series of consecutive hydroisomerization steps, each increasing the degree of branching [11–13]. If one simplifies this process by only considering methyl group branches, the hydroisomerization of an n-alkane of N carbon atoms can be described as illustrated in Figure 1.2.

In addition to the hydroisomerization reactions that change the degree of branching, there are also those that change the distribution of branching towards thermodynamic equilibrium (methyl shift) [15–18]. None of the hydroisomerization reactions equilibrate completely because they compete with consecutive hydrocracking reactions that decompose the isomers [12, 15–20]. The probability of a molecule undergoing a hydrocracking reaction increases with increasing degree of branching, because

$$n - C_N \rightleftharpoons Me - C_{N-1} \rightleftharpoons diMe - C_{N-2} \rightleftharpoons triMe - C_{N-3} \rightleftharpoons etc.$$
  
 $\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$   
 $Me - C_{N-1-M} \qquad Me - C_{N-1-M}$   
 $n - C_M \qquad Me - C_{M-1}$ 

**Figure 1.2:** n-Alkane hydroconversion. A linear alkane consisting of N carbon atoms  $(n-C_N)$  is first converted into branched isomers. The branched isomers can subsequently hydrocrack into smaller molecules [14].

more extensively branched isomers afford the formation of more stable carbocationic hydrocracking transition states (Figure 1.3) [13,15–18]. For n-alkanes as short as n-C<sub>10</sub> the sequential series of hydroisomerization reactions is interrupted at the trimethylheptane stage, since very few trimethylheptanes desorb intact [15,21]. The first reason for the extremely low trimethylheptane yield is that trimethylheptanes have a significantly higher gas phase Gibbs free energy of formation than the less branched isomers [22], so that they form only in relatively low concentration to begin with. A second reason for the extremely low trimethylheptane yield is that  $\alpha\alpha\gamma$ -trimethylheptanes hydrocrack significantly more rapidly than any dimethylalkane [13,15–18]. Furthermore, trimethylheptanes that are not an  $\alpha\alpha\gamma$ -trimethlheptane are only a few rapid methyl shifts away from forming an  $\alpha\alpha\gamma$ -trimethlheptane, which in turn readily undergo hydrocracking reactions.

The product distribution obtained from these reactions depends highly on the relative occurrence of the various isomers, because each isomers may serve as a reaction intermediate to a different set of products. The foundation of the shape selectivity imposed by zeolites on these reactions is their ability to alter the distribution of reaction intermediates by modifying their Gibbs free energy of formation and their Gibbs free energy barrier to diffusion. The influence of the zeolite structure on the Gibbs free energies depends critically on the pore topology, resulting in large differences in catalytic selectivity between pore topologies. These differences can be studied by analyzing the adsorption behavior of all molecules involved.

### 1.3 Hydrocarbon adsorption in zeolites

The absorption behavior of hydrocarbons in zeolites is usually quantified by means of the adsorption isotherm, which represents the amount of hydrocarbon adsorbed in a pressure range at a given temperature. For low pressures, there is a linear relation between the pressure p and the loading  $\theta$  (Henry's law):  $\theta = K_H \cdot p$  in which  $K_H$  is the Henry coefficient. This Henry coefficient is proportional to the Gibbs free energy of adsorption of a single molecule in an empty zeolite and expresses the affinity of a molecule for a particular pore system.

To show the effect of pore topology on the adsorption of single molecules, we have plotted the free energy of adsorption of various branched  $C_{10}$  isomers relative to decane (see Figure 1.4). Only small differences are found in the FAU-type



**Figure 1.3:** Important alkane (C<sub>10</sub>) reactions [14]. A, B<sub>1</sub>, B<sub>2</sub>, and C are  $\beta$ -scission cracking reactions, MS (methyl shift) and BR (branching) are isomerization reactions. The reactions are ordered according to their relative reaction rate (indicated by the number on the arrow) [14], with the  $\alpha\alpha\gamma$ -trimethlheptane (A) being the most reactive.

zeolite. This is because the FAU-type pore system comprises large (12 Å) spherical cages, in which all isomers can be accommodated with equal ease. Larger difference are observed in MFI-, MEL-, and TON-type zeolites. Especially the uni-directional 5 Å pores of TON-type zeolites have difficulty hosting the more bulky di-, and tribranched alkanes, which is reflected in a very high free energy of adsorption for these molecules. The subtlety of shape selective adsorption is nicely shown by the results of MFI- and MEL-type zeolites. Although both zeolites have comparable three-dimensional pore systems (intersecting channels of 5.5 Å), their preference for adsorbing dimethyloctane is quite different. MFI prefers 4,4-dimethyloctane while MEL prefers 2,4-dimethyloctane. Such differences can play an important role in adsorption and catalytic processes, as will be shown in chapter 4.

Thermodynamic data like these can not always be conveniently obtained from experiments. For example, the determination of adsorption isotherms of long-chain alkanes can be quite time consuming, requiring weeks of equilibration in the case of decane [23]. When mixtures of alkanes are considered, experiments become in-



**Figure 1.4:** The Gibbs free energy of adsorption of decane isomers relative to n-decane in FAU-, TON-, MFI-, and MEL-type zeolites as obtained from CBMC simulations. The changes in the Gibbs free energy were calculated using one molecule at infinite dilution at T=415 K.

creasingly complicated. Additionally, not always are the conditions of interest such that they are readily accessible without a complicated experimental setup (high temperature and pressure), or unwanted side-effects like chemical reactions. In some cases it is also not possible to obtain data on all reaction intermediates, since some intermediates can not diffuse inside the zeolite framework. Those locked in "ship-inthe-bottle" molecules can be important in determining the final product distribution, as will be shown in chapter 4. Computer simulations can provide an alternative way of obtaining the thermodynamic data in the aforementioned cases, with the added advantage of providing molecular information on the adsorbed molecules.

### 1.4 Simulations

Computer simulations may be a powerful and cost-effective tool to obtain molecular scale information of a system, provided that the interatomic interactions are described in an adequate manner and that the simulation method will produce accurate results in a reasonable amount of time.

In most zeolites there is a tight fit between the adsorbed alkanes and the zeolite wall. As a result, there are often high barriers present for diffusing molecules. Because of these diffusional barriers simulation methods that are based on the time evolution of a system (Molecular Dynamics (MD)) are not suited to obtain equilibrium properties like adsorption isotherms. Therefore the method of choice is the Monte Carlo (MC) method.

In a MC simulation, atom configurations are generated randomly. For each configuration the energy u is calculated. The probability of finding a generated configuration in the system is directly proportional to  $e^{-\beta \cdot u}$  where  $\beta = 1/(k_B \cdot T)$ ,  $k_B$  the Boltzmann constant and T the temperature in K. The decision to accept a new configuration in favor of the old one is made by comparing the "weights" of both configurations [24]. This procedure ensures a more homogeneous sampling of a system with large barriers.

But the same difficulties that make the use of MD for adsorption studies in zeolites hard, hamper also all but the most trivial MC based studies. The amount of empty space in a zeolite is only a small fraction of the total volume. To find a empty spot for a small molecule like methane already takes quite a few trials. Once the molecules get larger, the number of trials needed increases exponentially. As a result, the simulation of the adsorption of long-chain or branched paraffins with conventional molecular simulation techniques will require excessive amounts of CPU time.

We use the configurational-bias Monte Carlo technique (CBMC) to overcome this problem [24]. In CBMC an alkane molecule is grown atom-by-atom, in such a way that the empty spots are found. For each atom a set of k trial orientations is generated and the energy  $u_i(j)$  of each trial position j of atom i is computed. One of these trial positions is selected with a probability

$$p_i(j) = \frac{\exp[-\beta u_i(j)]}{\sum_{l=1}^k \exp[-\beta u_i(l)]} = \frac{\exp[-\beta u_i(j)]}{w(i)},$$
(1.1)

where  $\beta = 1/(k_B \cdot T)$ . The selected trial orientation is added to the chain and the procedure is repeated until the entire molecule has been grown. For this newly grown molecule the so-called Rosenbluth factor is computed

$$W(n) = \prod_{i} w(i). \tag{1.2}$$

A similar procedure can be used to compute the Rosenbluth factor of the old configuration W(o). The bias introduced by this growing scheme is removed exactly [24], if the conventional acceptance rule is replaced by

$$\operatorname{acc}(o \to n) = \min(1, W(n)/W(o)). \tag{1.3}$$

Using this scheme we can calculate thermodynamic properties of interest like the excess chemical potential  $\mu_{ex}$  of a molecule

$$\exp(-\beta\mu_{ex}) = \frac{\langle W \rangle}{\langle W_{id} \rangle},\tag{1.4}$$

where  $\langle W \rangle$  is the average Rosenbluth factor. The subscript *id* denotes an alkane molecule in the ideal gas phase, which can be calculated from a simulation of a single molecule in the gas phase. Properties of interest to adsorption studies, like the Gibbs free energy of adsorption  $\Delta G_{ads}$  (J/mol) and the Henry coefficient  $K_H$  (mol/kg Pa) can be calculated from the chemical potential using

$$\Delta G_{ads} = -R \cdot T \cdot \ln\left(\frac{\langle W \rangle}{\langle W_{id} \rangle}\right) \tag{1.5}$$

where R is the gas constant (8.3145 J/mol K) and

$$K_H = \frac{\langle W \rangle}{\langle W_{id} \rangle \cdot \rho_z \cdot R \cdot T}$$
(1.6)

where  $\rho_z$  is the zeolite framework density (kg/m<sup>3</sup>). Additionally the heat of adsorption q (J/mol) of a single molecule can be calculated from the average of the total energy  $\langle U_a \rangle$ 

$$q = \langle U_a \rangle - \langle U_a \rangle_{id} - R \cdot T \tag{1.7}$$

where  $\langle U_a \rangle_{id}$  is the average of the total energy of a molecule in the ideal gas phase.

The CBMC technique can also be used in the grand-canonical ensemble to obtain adsorption isotherms [24]. In this ensemble the number of molecules is allowed to fluctuate through exchanges between the zeolite and an imaginary molecule reservoir of known chemical potential and temperature. Complete isotherms are calculated by varying the chemical potential of the reservoir.

More details about the simulation model and technique are described in chapter 2.

# II Justification of the alkane-zeolite model<sup>1</sup>

A prerequisite for obaining meaningful results out of any type of molecular simulation is an adequate description of the interatomic forces. For some systems the use of general purpose forcefields will suffice, while in others the use of a tailor-made forcefield is required.

The study of the adsorption of alkanes in zeolites presents such a case where a tailor-made forcefield for the alkane-zeolite interaction is needed to reproduce all observations from adsorption experiments. For example CVFF-type forcefields are unable to reproduce the step in the isotherm of iso-butane adsorbed in MFI [28]. A custom design also allows for convenient approximations, like a rigid zeolite lattice and united atom descriptions of both the alkanes and the zeolites, that reduce the computational time considerably. Additionally, because of the large difference in operating conditions of the various zeolites applications, it is also important that the forcefield gives reasonable results over a wide range of temperatures and pressures.

### 2.1 Forcefield

In the forcefield used throughout this thesis, the alkanes are modeled using the united atom representation, i.e. the CH<sub>3</sub>, CH<sub>2</sub>, CH, and C groups are modeled as single interaction centers. The bond length between the atoms is kept fixed at 1.53 Å. The bond-bending is modeled by harmonic cosine potential

$$u^{bend} = \frac{1}{2} k_{\theta} [\cos(\theta) - \cos(\theta_{eq})]^2$$
(2.1)

with the equilibrium angle  $\theta_{eq} = 113^{\circ}$  and the force constant  $k_{\theta}/k_B = 85000.0$  K. The torsional angles are controlled by

$$u^{tors}(\phi) = \sum_{i=0}^{i=5} C_i cos^i(\phi)$$
 (2.2)

with the values of  $C_i$  listed in Table 2.3. The interaction of the atoms belonging to different molecules or to the same molecule but separated by more than three bonds,

<sup>&</sup>lt;sup>1</sup>This chapter is based on refs. [25–27]

**Table 2.1:** Parameters for the Lennard-Jones potential describing the interactions between atoms of an alkane [29–31].

$\epsilon/k_B/[K] \sigma/[Å]$						
$\overline{CH_4}$ - $CH_4$	148.0	3.73				
$CH_3$ - $CH_3$	98.0	3.75				
$CH_2$ - $CH_2$	46.0	3.95				
CH-CH	10.0	4.68				
C-C	0.5	6.40				

**Table 2.2:** Parameters for the Lennard-Jones potential describing the interactions between an alkane and a zeolite [33].

$\epsilon$	$/k_B/[K$	] <i>σ</i> / [Å]
$\overline{CH_4}$ -O	96.5	3.60
$CH_3-O$	80.0	3.60
$CH_2-O$	58.0	3.60
CH-O	58.0	3.60
C-O	5.0	3.60

**Table 2.3:** Torsion potentials for linear and branched alkanes. The torsion around the x - A - B - y axis is decribed using the functional form of equation 2.2 [34].

	A,B	$CH_2$ - $CH_2$	$CH-CH_2$	C-CH <sub>2</sub>	C-C	C-CH	CH-CH
	x,y	C,C	H,C	C,C	C,C	C,H	H,H
$\overline{C_0/k_B/[\mathrm{K}]}$		1204.654	1367.086	1293.324	2045.657	1575.127	1092.268
$C_1/k_B/[\mathbf{K}]$		1947.740	4360.147	3879.849	6136.797	4725.259	2822.786
$C_2/k_B/[K]$		-357.845	416.005	0.0	0.0	0.0	-908.033
$C_3/k_B/[K]$		-1944.666	-6499.427	-5173.163	-8182.447	-6300.384	-3007.027
$C_4/k_B/[K]$		715.690	-832.004	0.0	0.0	0.0	1816.066
$C_5/k_B/[K]$		-1565.572	1646.129	0.0	0.0	0.0	-1816.059

is described by a 12-6 Lennard-Jones potential

$$u^{lj}(r_{ij}) = 4\epsilon \left[ \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6 \right]$$
(2.3)

The Lennard-Jones parameters are shown in Table 2.1 [29–31]. Interactions between different atoms are computed using the Jorgensen mixing rules [32]:  $\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}$ ,  $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$ . The potentials are truncated at 13.8 Å, and tail corrections are applied [24].

The zeolite-alkane interactions are assumed to be dominated by dispersive interactions with the oxygen atoms of the zeolite framework. Apart from work presented in section 5 of this chapter, the zeolite is modeled as a rigid crystal [35] consisting exclusively of SiO<sub>2</sub>, so as to make the calculation of zeolite-alkane interactions efficient. This allows the use of special interpolation techniques [36, 37] to obtain the correct paraffin conformation at any given temperature. The Lennard-Jones parameters for the zeolite-alkane model have been fitted to the adsorption enthalpies and the Henry coefficients of linear and mono-branched alkanes in Silicalite-1 (MFI) [33]. The resultant forcefield reproduces the Henry coefficients, the changes in the free energy of formation (i.e. the free energy of adsorption), the adsorption enthalpies and isotherms for linear and mono-branched paraffins in Silicilite-1 [33].

### 2.2 Simulation Technique

For the calculation of the heats of adsorption and the Henry coefficient we perform Monte Carlo simulations in the *NVT* ensemble at infinite dilution (i.e. using a single particle). During such a simulation, trial moves are performed to insert an alkane at a random position inside the zeolite. We use the configurational-bias Monte Carlo technique to increase the acceptance ratio of these insertions [24]. Additionally trial moves are performed to translate, rotate, and partial-regrow a molecule at its place of insertion. For the calculation of adsorption isotherms we perform Monte Carlo simulations in the grand-canonical ( $\mu VT$ ) ensemble. In this ensemble, additional trial moves are performed to exchange molecules between a zeolite and a molecule reservoir of constant chemical potential. The number of trial moves for each simulation is in the order of 10<sup>6</sup>, the exact number being dependent on the size of the molecules (the larger, the more trial moves) and number of different molecules (a mixture takes longer to equilibrate).

In the remainder of this chapter we will focus on whether this forcefield, which is fitted on low pressure Silicilite-1 data, can be used at higher pressures and for other zeolite topologies and whether the assumption that the zeolite can be considered rigid is valid.

### 2.3 Adsorption in Silicalite-1

To verify the accuracy of the forcefield at higher pressures, we compare CBMC simulation results for pure component isotherms of hexane isomers with the experimental measurements of Cavalcante and Ruthven [38] and Millot et al. [39]; see Figure 2.1. The agreement between CBMC simulations and experimental data fits of these authors can be considered to be good for a wide range of pressures and temperatures.

### 2.4 Adsorption in other zeolites

The results presented in the previous section show that this forcefield is perfectly capable of reproducing experiments at both low and high alkane loading in Silicalite-1. The question remains whether this forcefield can also be used to simulate alkane adsorption in other zeolite topologies.

To answer this question we studied the adsorption of small alkanes ( $C_1 - C_3$ ) in a set of high silica zeolites with a wide range of pore-sizes, consisting of FER, TON, MTW, and DON (see Table 2.4). The results of the simulations at infinite dilution are given in Tables 2.5 and 2.6, the results for the adsorption isotherms are given in Figures 2.2, 2.3 and 2.4. In both cases the results are compared to experiments by Savitz et al. [40], Eder et al. [41] and Rees et al. [42]

**Thermodynamics:** As stated before, it is crucial to be able to reproduce both the Henry coefficient and the heat of adsorption (at infinite dilution) in order to correctly calculate adsorption over a range of temperatures. Since the Lennard-Jones parameter set of Vlugt et al. was fitted using data obtained on the zeolite MFI, we also include



**Figure 2.1:** Pure component isotherms of hexane isomers obtained at various temperatures: CMBC simulations vs experiments: (a) hexane, (b) 2,2-dimethylbutane, (c) 2-methylpentane and (d) 3-methylpentane. The open symbols represent simulation data, the closed symbols represent experimental data. The lines serve as a guide to the eye.

zeolite	topology	oxygens in ring	pore dimensions / [Å]
FER	2-D	10,8	5.4 x 4.2, 4.8 x 3.5
TON	1 <b>-</b> D	10	5.7 x 4.6
MFI	2-D	10,10	5.6 x 5.3, 5.5 x 5.1
MTW	1 <b>-</b> D	12	6.0 x 5.6
DON	1-D	14	8.2 x 8.1

Table 2.4: Pore dimensions of zeolites. [2]

	-Q <sub>st</sub> /[kJ/mol]				
Zeolite	$CH_4$	$C_2H_6$	C <sub>3</sub> H <sub>8</sub>		
	sim exp ref	sim exp ref	sim exp ref		
FER	21.6 27.7 [40]	34.2 41.7 [40]	43.9 53.3 [40]		
			49 [41]		
TON	21.0 27.2 [40]	32.1 39.0 [40]	42.0 48.8 [40]		
		31.9 [42]	42.0 [42]		
			49 [41]		
MFI	20.0 20.9 [40]	30.4 31.1 [40]	39.1 41.4 [40]		
	20 [43]	33 [43]	40 [43]		
	18.6 [44]	30.7 [44]	40.9 [44]		
		32.8 [45]	39.9 [45]		
MTW	18.8 20.9 [40]	29.2 29.5 [40]	38.8 37.6 [40]		
DON	13.4 14.2 [40]	20.1 22.2 [40]	26.0 28.1 [40]		

**Table 2.5:** Zero-coverage heats of adsorption. Comparison between this work (sim) and experiments (exp) at 25 C.

				$K_H/[mm$	ol/g/Pa]		
Zeolite	T(K)	$CH_4$		$C_2H_6$		C <sub>3</sub> H <sub>8</sub>	
		sim	exp	sim	exp	sim	exp
FER	309	$7.2 \times 10^{-6}$	$2.0 \times 10^{-5}$	$1.9 \times 10^{-4}$	$7.2 \times 10^{-4}$	$9.1 \times 10^{-4}$	
TON	298	$5.4 \times 10^{-6}$		$9.2 \times 10^{-5}$	$9.1 \times 10^{-5}$	$6.8 \times 10^{-4}$	$7.0 \times 10^{-4}$
TON	309	$4.0 \times 10^{-6}$	$6.8 \times 10^{-6}$	$5.8 \times 10^{-5}$	$1.4 x 10^{-4}$	$3.7 \times 10^{-4}$	
MFI	309	$8.3 \times 10^{-6}$	$6.3 \times 10^{-6}$	$1.6 \times 10^{-4}$	$1.2 \times 10^{-4}$	$1.5 \times 10^{-3}$	
MTW	309	$3.7 \times 10^{-6}$	$4.0 \times 10^{-6}$	$8.8 \times 10^{-5}$	$9.3 \times 10^{-5}$	$1.1 \times 10^{-3}$	
DON	309	$1.3 \times 10^{-6}$	$3.2 \times 10^{-6}$	$1.2 \times 10^{-5}$	$1.6 \times 10^{-5}$	$7.9 \times 10^{-5}$	$1.1 \times 10^{-4}$

**Table 2.6:** Henry's Constants. Comparison Between This Work (sim) and Experiments (exp) from ref [40] at T=309 K.



**Figure 2.2:** Adsorption isotherms for methane, ethane, and propane in FER-type zeolites. The open symbols represent simulation data, the closed symbols represent experimental data. The lines serve as a guide to the eye.

results for the heat of adsorption and Henry coefficient for this zeolite in tables 2.5 and 2.6.

The experimental results for the widely studied zeolite MFI presented in table 2.5 show quite some variation. If we use the scatter of the experimental data for MFI as a measure for the typical experimental uncertainties, we should allow for an uncertainty of 2 kJ/mol. If we take this uncertainty into account, comparison of the simulation data with the experimental data shows satisfactory agreement for the zeolites MTW, DON, and TON of Rees et al. For FER and TON of Savitz et al. and Eder et al. , the agreement is less satisfactory. The results for the Henry coefficient show a similar trend (see table 2.6), with one exception: The results for the Henry coefficient for TON are in quite good agreement with the experimental results of both Savitz et al. and Rees et al. Also the results for the isotherms show the same trend. The agreement between our simulations and the experiments is in general good for TON, MTW, and DON, and again somewhat less for FER.

A reason for the deviation of our simulation results for the heats of adsorption from the experimental data may be Si/Al ratio of the samples used in case of the experiments for FER and TON by Savitz et al. and Eder etal. For each aluminium there is also a hydrogen atom present. Eder et al. have shown that these hydrogen atoms can give a negative contribution to the heat of adsorption of up to 10 kJ/mol in the case of H-MFI [46] and 7 kJ/mol in the case of H-TON (Si/Al=52) [41]. Because the TON sample of Savitz et al. has the same Si/Al ratio of 52, the deviation for the heat of adsorption can be attributed to the presence of acid-sites. This is confirmed by the experimental results by Rees et al. (who use an all-silica version of TON) that agree very well with our simulation results.



**Figure 2.3:** Adsorption isotherms for methane, ethane, and propane in TON-type zeolites. The open symbols represent simulation data, the closed symbols represent experimental data. The lines serve as a guide to the eye.



**Figure 2.4:** Adsorption isotherms for methane, ethane, and propane in DON- (left) and MTW-type (right) zeolites. The open symbols represent simulation data, the closed symbols represent experimental data. The lines serve as a guide to the eye.

A reason for the deviation of the simulated adsorption isotherms from the experimental one in the case of FER could be the sensitivity of the Lennard-Jones potential for small changes in the parameters when the oxygen and carbon groups are in close proximity. This effect would be the largest in the case of FER, since this zeolite has the narrowest pore system of all zeolites under evaluation. The parameters fitted on MFI can be less than optimal, resulting in a deviation for FER. Interestingly, other studies found a similar deviation from experimental results using a different forcefield [47].

**Siting:** We examined the preferential adsorption sites of the alkanes in the zeolites. For each zeolite the siting is illustrated in the Figures 2.5, 2.6, and 2.7 in the form of density distributions. These distributions are constructed by plotting the position of the centers of mass of the molecules in the simulation box at fixed intervals throughout the simulation. The density of the dots is a measure of the probability of finding the center of mass of a particular molecule at a given position.

From these figures we obtain information on the location of the adsorption sites. Thus, Figure 2.5 shows the siting of propane in FER at low and high pressure. At low loadings propane preferentially adsorbs in the small cages, accessible through the 8-ring windows. At high pressures propane adsorbs in both the cages and the 10-ring channels. This observation compares nicely to the results of NMR experiments performed by Van Well et al. [47,48]. Similar results were obtained in the computational part of their study [47,48] using a slightly different forcefield from the one used in this study.

In Figure 2.6 the undulations in the channels of TON can be observed as the methane molecules adsorb homogeneously throughout the channels. These undulations give rise to (in)commesurate diffusion of double branched alkanes, which is



**Figure 2.5:** Density distribution of propane in FER in the Henry regime (a) and at 500 kPa (b) at T=309 K.



(a) bc plane

(b) ab plane

**Figure 2.6:** Density distribution of methane in TON at 500 kPa, T=309 K projected on the bc plane (a) and ab plane (b).



Figure 2.7: Density distribution of ethane in DON (a) and MTW (b) at 500 kPa, T=309 K.

highly dependent on the spacing between the methyl groups (as is shown in chapter 4).

The difference in pore size between the uni-directional pores of DON and MTW is reflected in the distribution of adsorbed ethane, as shown in Figure 2.7. The pore wall of MTW forces the ethane molecules to adsorb at the center of the pore. In DON, the pore is of such a size that the ethane molecules adsorb to the wall, leaving the center of the pore unoccupied. This difference in available space is also reflected in the maximum adsorption capacity of both zeolites.

### 2.5 The influence of framework flexibility on adsorption

Computer simulations of adsorption of hydrocarbons in zeolites are usually performed using rigid zeolite frameworks (as is the case throughout the rest of this thesis). This has two big advantages in terms of the speed of the computations: (1) It allows for the use of grid interpolation techniques to compute the hydrocarbonzeolite interaction very efficiently. (2) No Monte Carlo cycles are used to change the conformation of the zeolite.

Because of the increasing amount of available computer power in the last few years, it is now possible to investigate whether the rigid framework approximation is valid. For molecular dynamics simulations, it is generally believed that the influence of the flexibility is rather small for molecules that are small compared to the pore diameter of the zeolite [49,50], but much larger for hydrocarbons that fit tightly into the channels of the zeolite. For example, the diffusivity of aromatics in Silicalite changes

an order of magnitude if the framework flexibility is taken into account [51]. Similar effects have been found for butane and isobutane in Silicalite [52]. Auerbach and co-workers found that the framework flexibility has only a small influence on the site-to-site jump constant for benzene in zeolite NaY. Instead, a much larger influence on the energy dissipation of a single benzene molecule was found [53]. Framework flexibility effects might also be present for molecules in cation-containing zeolites where vibrations of the framework, cation, and adsorbate are strongly coupled [53]. For a review of recent molecular dynamics simulations in zeolites, we refer the reader to refs. [54–57].

Also for the adsorption of hydrocarbons, it is generally believed that flexibility is only important if the adsorbate fits tightly into the zeolite pore, for example, for light hydrocarbons in the zeolite DD3R [58] or for aromatics in Silicalite [59]. For different alkane-zeolite potentials, the Henry coefficient of linear alkanes in the zeolite Silicalite as a function of the number of carbon atoms is always a linear function, while experiments show a systematic decrease for longer chains [33]. Previously, this effect has been attributed to the flexibility of the framework [33].

In this section, we investigate the influence of framework flexibility on the adsorption properties of linear and mono-branched (2-methyl) hydrocarbons in the wellstudied zeolite Silicalite-1. The adsorption of hydrocarbons in this zeolite is of special interest because it has been suggested that Silicalite membranes are capable to separate linear and branched hydrocarbons [27, 60–66]. To incorporate the flexibility of the zeolite framework, we need to have an additional forcefield describing the interactions between the zeolite atoms. The disadvantage of some zeolite forcefields is that by changing the forcefield parameters, not only the flexibility but also the framework structure changes, i.e. the average positions of the zeolite atoms in a simulation using a flexible zeolite framework may or may not correspond to the zeolite crystal structure. To save computer time we would like to use forcefield which is as simple as possible, which means that we would like to avoid (if possible of course) the use of electrostatic interactions which requires an Ewald summation or similar method [24]. Therefore, one has to choose this forcefield carefully, which we will do in the next section.

#### 2.5.1 Models for flexible zeolite frameworks

Using the model of Demontis [67] et al., we have constructed a model where the flexibility is taken into account explicitly without destroying the zeolite structure. There are several forcefields that can describe the flexibility of the zeolite framework, see ref. [54] for an excellent review. The forcefield of Kramer and co-workers describes the O-O and Si-O interactions by a Buckingham potential with a Coulomb term and does not include any non-coulombic Si-Si interactions [68, 69]. This forcefield has the disadvantage that a computationally expensive Ewald summation is necessary to compute the interactions correctly. Furthermore, it is not trivial to tune the degree of flexibility of this model. Therefore, we have focused our attention to the conceptually simpler model of Demontis and co-workers [67]. In this forcefield, simple harmonic potentials are used between Si-O and O-(Si)-O bonds,

$$V_{Si-O}(r) = k_{Si-O} \times (r - r_{0,Si-O})^2$$
(2.4)

$$V_{O-O}(r) = k_{O-O} \times (r - r_{0,O-O})^2$$
(2.5)

in which  $r_{0,Si-O} = 1.605$  Å and  $r_{0,O-O} = 2.61786$  Å are the equilibrium bond lengths and  $k_{Si-O}$  and  $k_{O-O}$  the spring constants. To reduce the number of parameters, we have chosen  $k = k_{O-O} = 0.2 \times k_{Si-O}$  (which is approximately the case for the original model) and only varied  $k_{O-O}$ . It is important to note that in this model, the parameters  $r_{0,Si-O}$  and  $r_{0,O-O}$  are constant for all bonded pairs and that only nearest neighbors are considered. As no other pair contacts are involved, the initial topology of the framework bonds is conserved during a computer simulation. The spring constants and equilibrium bond lengths of these potentials have been fitted to reproduce the IR spectrum of the zeolite Silicalite. In the original model, the values of these parameters are  $k_{O-O}/k_B = 2.6 \times 10^4$  KÅ<sup>-2</sup> and  $k_{Si-O}/k_B = 1.3 \times 10^5$  KÅ<sup>-2</sup>. Also in this model, there are no direct Si-Si interactions.

The key difference between the models is that the model of Kramer and co-workers does not use any topological information about the Si-O bonds of the zeolite, while this topology is explicitly present in the model of Demontis et al.

In principle, the flexibility of both models can be tuned by changing the parameters in the models. It is very important to note that this may also influence the structure of the zeolite. As we will show later, this makes the comparison between these models and a rigid framework based on the crystal structure quite unfair. It seems reasonable that framework flexibility can be taken into account by relatively simple potentials. However, it is not obvious at all that relatively simple harmonic potentials with fixed equilibrium bond lengths can correctly predict the equilibrium (crystal) structure of a zeolite (see, for example, ref. [70]). As we know already the crystal structure from experimental data, this may not be necessary. Therefore, we have also investigated a new model in which the equilibrium distances  $r_{0,O-O}$  and  $r_{0,Si-O}$  are no longer constants. Instead, these values have been taken directly from the crystal structure and therefore vary for different bonds. This reduces the spring constant k to some sort of potential-of-mean-force constant which describes the fluctuations around the crystal structure. The minimum energy structure (which is the crystal structure) is reproduced exactly when  $T \to 0$  or  $k \to \infty$  and the harmonic potentials are describing fluctuations around this equilibrium structure. We will call this model the modified Demontis model. Note that we did not consider the even simpler Einstein crystal [24], as we expect correlation effects between neighboring oxygen atoms in the zeolite.

To simulate a flexible zeolite, we have included MC trial-moves that attempt to give a randomly selected zeolite atom a random displacement. The maximum displacement of zeolite atoms was adjusted in such a way that 50% of all displacements were accepted. As the number of zeolite atoms is much larger than the number of hydrocarbon molecules in the zeolite, the number of attempted zeolite displacement was chosen in such a way that it was two orders of magnitude larger than the number of attempts to displace a hydrocarbon molecule. It is important to note that the volume of our simulation box is constant, i.e. we neglect the influence of the flexibility on the equilibrium framework density. We have taken the crystal structure of Silicalite (2x2x4 units cells) from the Cerius<sup>2</sup> package [71], resulting in 4608 zeolite atoms. A typical simulation takes at least 10 times more CPU time than a comparable simulation for a rigid zeolite.

#### 2.5.2 Results and Discussion

Zeolite Structure. To study the different models for zeolite flexibility, we have performed simulations of a flexible zeolite without any hydrocarbon molecules adsorbed. The starting point of these simulations was the original crystal structure. To avoid large fluctuations we performed our simulations using a fixed center of mass. In Figure 2.8, we have plotted the RMS fluctuations of the oxygen atoms around their average positions, as well as the RMS deviation between the crystal structure and the average zeolite structure as a function of the flexibility  $k/k_B$ . The RMS fluctuations are smaller than a typical bond length between zeolite atoms. For the Demontis model with fixed equilibrium bond lengths, the RMS fluctuations are approximately constant when  $k/k_B > 10000 \text{ K}\text{\AA}^{-2}$ , while these fluctuations go to zero for large values of  $k/k_B$  for the modified Demontis model. Therefore, it seems that the Demontis model still has some flexibility even for very large values of  $k/k_B$ , while for the modified Demontis model the flexibility can be easily tuned without changing the RMS difference with the crystal structure too much. Furthermore, in the limit of  $k \to \infty$  (or  $T \rightarrow 0$ ) the average structure of the Demontis model does not converge to the exact crystal structure. For low values of  $k/k_B$  (< 1000 KÅ<sup>-2</sup>), the differences between the average structure and the crystal structure become very large. At these conditions, adsorption data are no longer meaningful.

To further illustrate this effect, in Figure 2.9 we have plotted the Henry coefficient of the different models as a function of the framework flexibility. Clearly, there is a significant difference between the original Demontis model and the rigid zeolite framework. We have found similar differences for the heat of adsorption. Note that as the Henry coefficient is plotted on a logarithmic scale, a small deviation from the experimental value gives already a significant deviation in the adsorption isotherm. We found that for all hydrocarbons considered in this study, the Henry coefficient as well as the heat of adsorption is equal or lower than those for a rigid zeolite framework. Because of the results presented in Figure 2.9, in the remainder of this paper we will only consider the modified Demontis model with equilibrium bond lengths taken directly from the crystal structure.

Henry coefficients and heats of adsorption In Figure 2.11, we have plotted the Henry coefficient and the heat of adsorption for linear alkanes in Silicalite as a function of the number of carbon atoms for various framework flexibilities. In our plots, we have also included some experimental data for this system taken from the overview given in refs. [33, 72]. Clearly, we observe straight lines for all data sets, except the experimental data set for the Henry coefficient. Note that also for other alkane-zeolite forcefields straight lines are observed [73]. This means that we cannot attribute this earlier experimentally observed deviation from a straight line to



**Figure 2.8:** RMS differences and fluctuations for the original model of Demontis (left) and the new model (right) as a function of the flexibility  $k/k_B$ . Circles: RMS deviation from the average position. Squares: RMS difference between the crystal structure and the average structure in the simulation. The average structure was computed using a fixed center of mass (see ref. [24]). T=300 K.



**Figure 2.9:** Henry coefficient *H* of n-hexane for various models as a function of the framework flexibility. Circles: model of Demontis et al. (original parameter:  $k/k_B=2.6 \times 10^4$  KÅ<sup>-2</sup> [67]). Squares: modified Demontis model. The dashed line represents the Henry coefficient for a rigid zeolite. *T*=300 K.



**Figure 2.10:** Schematic representation of the zeolite Silicalite-1 (MFI). Straight channels (y direction) and zigzag channels (in the x-z plane) cross each other at the intersections.

the flexibility of the zeolite framework [33]. A possible explanation would be that at room temperature, the Henry regime for  $n-C_6$  and longer alkanes is only observed at such low pressures that experiments become inaccurate. If one assumes a Langmuir adsorption isotherm, computing an Henry coefficient at a pressure which is too large results in a systematic underestimation of the Henry coefficient.

For branched (2-methyl) alkanes, we also observe a linear relationship between the heat of adsorption and the Henry coefficient, see Figure 2.12. Note that there is little difference in these properties between linear alkanes and their monobranched isomers.

To quantify the influence of the flexibility on the thermodynamic data at low loading, we have plotted in Figure 2.13 the relative deviation d from the rigid framework of both the heat of adsorption and the logarithm of the Henry coefficient (represented by the function f),

$$d(k/k_B) = 1 - \frac{f(k/k_B) - f(k/k_B \to \infty)}{f(k/k_B \to \infty)},$$
(2.6)

Apparently, the differences are at most around 10% for the heat of adsorption and the Henry coefficient. For the lowest value of  $k/k_B$  (here: 500 KÅ<sup>-2</sup>), there is already a significant change in the zeolite structure (see Figure 2.8), but the heat of adsorption and Henry coefficient hardly change. Only for the Henry coefficients of ethane and long-chain hydrocarbons, these deviations seems to be somewhat larger. This is due to the fact that we compare the logarithm of the Henry coefficient. Therefore, the effect of the framework flexibility on the thermodynamic properties at low loading seems to be quite small, even for branched alkanes that have a tighter fit in the zeolite than linear alkanes.

Adsorption Isotherms To investigate the effect of framework flexibility at high loadings, we have computed the adsorption isotherms of  $n-C_4$ ,  $i-C_4$ ,  $n-C_7$ , and  $i-C_7$ , see Figure 2.14. The differences between the isotherms are striking. For butane (top, left), the isotherms show a Langmuir-like behavior with a maximum loading of approximately 1.6 mmol/g. This corresponds to slightly more than 9 molecules per



**Figure 2.11:** Henry coefficient (left) and heat of adsorption (right) for linear alkanes in Silicalite as a function of the number of carbon atoms. See refs. [33,72] for an overview of the available experimental data. *T*=300 K.



**Figure 2.12:** Henry coefficient (left) and heat of adsorption (right) for branched (2-methyl) alkanes in Silicalite as a function of the number of carbon atoms. T=300 K.



**Figure 2.13:** Relative differences (Eq. 2.6) between the Henry coefficients (left) and heats of adsorption (right) as a function of the flexibility  $k/k_B$ . *T*=300 K.

unit cell. There seems to be hardly any influence of the framework flexibility on the adsorption isotherm, except for the somewhat lower loading for  $k/k_B = 3000 \text{ K}\text{\AA}^{-2}$ , which is due to a lower Henry coefficient. For its branched isomer, isobutane (top, right), however, we find an inflection in the isotherm. In earlier studies, it was found that this inflection is due to the preferential adsorption of isobutane at the intersections of Silicalite [74], see also Figure 2.10. At 4 molecules per unit cell, all intersections are occupied and additional molecules can only be located in the straight- and zigzag channels. However, this requires an additional force which causes the inflection in the isotherm. This inflection has also been observed experimentally [43,44,75]. The effect of the framework flexibility on the inflection behavior is quite significant, at lower values of  $k/k_B$  this inflection seems to disappear. Note that even for  $k/k_B$  = 20000 KÅ $^{-2}$ , the minimum pressure to put more than 4 molecules per unit cell into the zeolite differs from the value of the rigid framework. For heptane (bottom, left), there is also an inflection in the isotherm around 4 molecules per unit cell. This is due to the commensurate freezing effect discovered by Smit and Maesen [76]. As the size of a heptane molecule is commensurate with the size of the zigzag channel in Silicalite (see Figure 2.10), we observe a freezing transition at high loading which causes entrapment of heptane molecules in this channel. Also for this system, the inflection becomes more pronounced for larger values of  $k/k_B$ . For isoheptane (bottom, right), the maximum loading is much lower than for heptane. The effect of the framework flexibility at medium loading is larger than for butane due to a higher Henry coefficient.

In Figure 2.15, we have plotted the adsorption isotherm of a 50% - 50% mixture of 2-methylpentane and n-hexane. In our earlier studied using a rigid zeolite, we found that at high pressures the branched component is excluded from the zeolite [27, 61].



**Figure 2.14:** Adsorption isotherms of  $C_4$  (top) and  $C_7$  (bottom) isomers for various flexibilities. Left: *n*-alkanes. Right: branched (2-methyl) alkanes. *T*=300 K.

For a flexible zeolite, we find the same effect. At large flexibilities and high pressures, the adsorption of the branched component is approximately three times larger that for the rigid framework.

It is interesting to speculate about the reasons why the influence of framework flexibility is so large for isobutane and heptane at higher loading. These systems have two different adsorption sites that have an occupation that depends on the pressure (or loading) of the system. At high loadings, there is a subtle interplay between these adsorption sites. For example, for isobutane, there is a minimum pressure required to get a few molecules into the channel interiors. This interplay can easily be disturbed by small fluctuations of the zeolite structure. If a channel interior is a bit smaller than in the crystal structure, no isobutane molecule will be adsorbed at this position. If, however, the channel interior is slightly larger an additional isobutane molecule will be able to adsorb and the structure will slightly modify around this molecule to give this molecule some extra space. This would explain the less pronounced inflection behavior of isobutane at low values of  $k/k_B$ . In the case of the 50% - 50% mixture of 2-methylpentane and n-hexane, the preference of the branched isomer for the intersections is so strong that small changes in zeolite structure do not change the competition between linear and branched isomers too much.

### 2.6 Conclusions

To verify the accuracy of our forcefield, we compared our simulation results at both low and high alkane loadings with experimental measurements on various zeolites. There is a good agreement between the experimental data and the simulations. In addition we find that the assumption that a zeolite can be modelled as a rigid crystal is valid, especially within the context of this thesis.



**Figure 2.15:** Adsorption isotherms of a 50% – 50% mixture of 2-methylpentane and n-hexane. Top left:  $k/k_B$ =3000 KÅ<sup>-2</sup>. Top right:  $k/k_B$ =20000 KÅ<sup>-2</sup>. Bottom:  $k/k_B$ =500000 KÅ<sup>-2</sup>. T=300 K.
# $$\label{eq:stars} \begin{split} & \textbf{III} \\ & \textbf{The adsorption of alkanes at elevated} \\ & \textbf{pressures}^1 \end{split}$$

In this chapter we focus on adsorption at higher pressures and especially on how the adsorption is influenced by the presence of other molecules in the zeolite. The adsorption behavior at low pressures is determined by the fit of molecules in the pore system, but once intermolecular forces come in to play life gets considerable more intriguing. By calculating adsorption isotherms one can identify the driving forces that determine the adsorption behavior.

## 3.1 Single component isotherms

The shape of an adsorption isotherm is determined by two configurational effects: (1) the number and energetics of preferential adsorption sites and (2) packing efficiencies at higher pressures. Figure 3.1 shows the adsorption isotherms of three C<sub>6</sub> isomers, n-hexane (hex), 2-methylpentane (3MP), and 2,2-dimethylbutane (22DMB), in MFI and AFI respectively. The figures clearly show the influence of both factors in two distinctly different zeolites topologies. MFI comprises intersecting straight channels and zig-zag channels, both with a diameter of 5.5 Å. AFI, on the other hand, has uni-directional pores with a diameter of 7.4 Å.

n-Hexane has no clear preferential adsorption sites in either of the two zeolites. In other words at all pressures n-hexane is adsorbed throughout the entire structure. This is also shown by the absence of steps in the isotherms. A similar smooth curve and distribution is found for both 3-methylpentane and 2,2-dimethylbutane in AFI. In contrast, for MFI a clear step is present in the 3MP isotherm. This inflection in the isotherm is caused by the preferential adsorption of the somewhat more bulky 3MP molecules at the intersections. The inflection occurs at a loading of 4 molecules per unit cell, which corresponds to the presence of 4 intersections per unit cell. When all intersections are occupied an extra force is needed (in the form of extra pressure) to push additional 3MP molecules in the energetically less favorable positions in between the intersections. 22DMB shows the same preferential adsorption at the intersections, but 22DMB has no inflection in the isotherm. This is because 22DMB is more bulky than 3MP and therefor the additional adsorption sites accessible to 3MP are not

<sup>&</sup>lt;sup>1</sup>This chapter is based on refs. [27,77]



**Figure 3.1:** Simulated pure component isotherms for n-hexane, 3-methylpentane, and 2,2dimethylbutane in MFI (left, T=362 K) and AFI (right, T=403 K).

accessible to 22DMB. The maximum loading of 22DMB in MFI is therefor restricted to 4 molecules per unit cell.

There are also large difference between both zeolites in the maximum loading for each component. In MFI, hexane has the highest maximum loading, followed by 3MP and 22DMB. The opposite is observed in AFI, were 22DMB has the highest maximum loading, and hexane the lowest. The differences are due to configurational entropy effects; molecules with the highest packing efficiency will be adsorbed most. Hexane can easily adsorb everywhere in the MFI structure. As a result, hexane molecules will be adsorbed until the pore-system is completely full. On the other hand, 3MP and 22DMB can only adsorb at certain sites. This restriction on the number of possible configurations means that not all of the available space can be filled with molecules. The difference in configurational entropy between linear and branched alkanes in MFI is clearly shown in a snapshot of a 50-50 mixture of hexane and 3MP (Figure 3.2). In AFI there are no preferential adsorption sites, so the highest loading is achieved by the molecule that packs most easily along a line. 22DMB is the most compact molecule of the three, hence has the highest maximum loading. Figure 3.3 shows a molecular picture of this length entropy effect.

## 3.2 Multi component isotherms

The configurational effects discussed in the previous section play an important role in adsorption behavior of mixtures. Figure 3.4 shows the adsorption isotherms of 50-50 mixture of n-hexane and 22DMB in MFI and AFI at T = 403 K. At low loadings both components adsorb according to their Henry coefficient, but at high loadings one of



**Figure 3.2:** Typical snapshot showing the location of a 50-50 mixture of  $nC_6$ -3MP at 362K and 100 Pa. Preferential siting of 3MP alkanes at the intersections between the straight and the zigzag channels is evident. The linear alkane can be located at any position within the silicalite structure.



**Figure 3.3:** Right: The snapshot shows some typical conformations of linear and branched hexane isomers in AFI. Left: The projected end-to-end distance distribution of n-hexane and 22DMB, the arrows indicate the effective size of the molecules.



**Figure 3.4:** Simulated adsorption isotherm of an equimolar mixture of 22DMB and  $n-C_6$  in MFI- (left) and AFI-type (right) silica, T=403 K.

the components is expelled from the zeolite. In MFI the linear molecule wins because it is not restricted to adsorption at the intersections, like 22DMB is (see Figure 3.2). Energetically, it is more efficient to obtain higher mixture loadings by replacing the 22DMB with n-hexane; this configurational entropy effect is the reason behind the maximum in the 22DMB loading in the mixture. In AFI the selectivity is reversed in favor of 22DMB because of the length entropy effect; A higher mixture loading can be obtained by absorbing the most compact molecules. The reader is referred to ref. [27, 66, 77] for a more extensive review of the entropy effects during sorption of alkanes in zeolites.

In the next section these entropy effects are used to rationalize Silicalite mebrane permeation data from Funke et al. [60] and Gump et al. [63]

# 3.3 Separation of alkane isomers by exploiting entropy effects

The separation of isomers of alkanes is a problem that is growing in industrial importance. New reformulated gasoline specifications are forcing petroleum refiners to reduce the amount of olefins and aromatics in gasoline and, consequently, there is a greater need in the refining industry for catalytic isomerization for converting straight chain hydrocarbons to branched hydrocarbons. Branched hydrocarbons are preferred to straight-chain hydrocarbons as ingredients in petrol because branched hydrocarbons burn more efficiently and have a higher octane number. Consider, for example, the isomers of hexane; n-hexane has a RON (Research Octane Number) = 30 whereas the corresponding RON values for its isomers are: 2-methylpentane (2MP) = 74.5; 3-methylpentane (3MP) = 75.5; 2,2-dimethylbutane (22DMB) = 94; 2,3-

dimethylbutane (23DMB) = 105. In the catalytic isomerization process, straight-chain hydrocarbons are converted to their mono- or di-branched structures. However, the product of catalytic isomerization is a mixture of linear and branched hydrocarbons that are in thermodynamic equilibrium and the separation of linear hydrocarbons from their branched isomers becomes necessary. The separation of the hydrocarbon isomers is usually carried out using adsorption in a bed of zeolite 5A particles [78,79] in which the principle of separation is that of molecular sieving. Only the linear paraffin is capable of entering the pores of 5A zeolite and the branched isomers are excluded. One important disadvantage of sorption separation using 5A zeolite is that the diffusivities, and hence the fluxes are very low. Therefore equipment sizes are large. Our research focus is the separation of alkane isomers by exploiting subtle entropy effects. A careful examination of the physical properties of linear and branched alkanes [80], shows that the largest difference between the properties of alkanes isomers is with respect to the freezing point. When a mixture of say n-C<sub>6</sub> and 2MP is cooled the first crystals to form will be that of the linear isomer. The reason is that the linear paraffin molecules "stack" more easily. Branching destroys the symmetry required for crystal formation. In other words the differences in the freezing points is due to differences in "ordering" or "packing" efficiencies. The major drawback in applying this principle to separate linear and branched alkanes in the gasoline boiling range is that the temperatures to which the mixtures must be cooled is very low, of the order of 120-180 K. Therefore freeze crystallisation is not a viable technological solution for separation of isomers in the 4-7 carbon atom range. Ideally we would like to be able to exploit packing efficiency, or configurational entropy, differences without the need to cool to such low temperatures required for crystallisation. To achieve this goal we consider adsorption of the alkane isomers inside the matrix of an ordered structure, such as that of silicalite-1. Silicalite consists of straight channels and zig-zag channels, which cross each other at intersections. The length of the normal hexane molecule, for example, is commensurate with the length of the zig-zag channel, between two intersections [76]. That the linear molecules pack more efficiently within the silicalite structure is also evidenced by the differences in the saturation loadings, expressed in molecules per unit cell, between linear and branched alkanes in silicalite; see Figure 3.5. We aim to demonstrate in this section that for mixtures of linear and branched alkanes, such differences in "packing" efficiencies could cause an almost total exclusion of the branched isomer. In order to demonstrate our entropydriven sorption separation of alkane isomers using medium pore-size silicalite, we need to be able to estimate the sorption characteristics of various mixtures of linear and branched alkanes in the 5-7 carbon atom range, of interest as components in gasoline. While there is a considerable amount of published experimental data on pure component isotherms for various alkanes and iso-alkanes [38,39,75,81,82], there is little or no experimental data on mixture isotherms. This lack of mixture isotherm data is most probably due to the difficulty of experimentation. In this section we discuss a strategy for generating the required mixture isotherms using Configurational-Bias Monte Carlo (CBMC) simulations. The study reported here is not only of technological importance in the context of isomer separation but emphasises some new scientific principles governing sorption of molecules in confined environments such as zeolites



**Figure 3.5:** Saturation loadings (molecules/unit cell) of alkanes in silicalite-1 obtained from CBMC simulations at T = 300 K.

and other nanoporous materials.

It is worthwhile describing the overall structure and strategy to be adopted in this section to give some perspective to the individual subsections. Firstly, the entropydriven separation principle is demonstrated by carrying out mixture simulations for isomers. We seek verification of the entropy separation principle by analysing published silicalite membrane permeation data of Funke et al. [60] and Gump et al. [63]. Subsequently, we examine mixtures of linear and branched alkanes where the constituents have different number of carbon atoms. It is important to remark here that we had first introduced the entropy-driven separation concept in an earlier short communication [83]; the current communication represents a fuller account of this concept and demonstrates its generic character. Furthermore, since the publication of our short communication, new experimental data on permeation of alkane isomers across a silicalite membrane have been published by Gump et al. [63]. To rationalise their experimental data, we performed many more simulations with various mixtures under a variety of temperature, pressures and compositions. Our simulations offer a fundamental explanation of their experimental results which is different to that presented by Gump et al. themselves.

## 3.3.1 CBMC simulation results for pure components and mixtures

**Pure component isotherms of hexane isomers.** We first consider the isomers n-hexane  $(n-C_6)$ , 2-methylpentane (2MP), 3-methylpentane (3MP) and 2,2-dimethylbutane (22DMB). The pure component isotherms at various temperatures are shown in Figures 3.6 (a), (b), (c) and (d). A good description of the pure component isotherms can be obtained with the Dual-site Langmuir (DSL) model [84]. Details on the fitting procedure as well as the fitted parameters can be found in ref. [27]. The fitted DSL



**Figure 3.6:** Pure component isotherms of hexane isomers obtained at various temperatures using CBMC simulations.

model is also shown in Figure 3.6. It is to be observed that n-C<sub>6</sub> shows a slight inflection at  $\Theta = 4$  due to commensurate freezing [76]. The branched isomers 2MP and 3MP also show an inflection at  $\Theta = 4$  for some temperatures because these molecules prefer the intersections between the straight and zig-zag channels of silicalite; to push them into the channel interiors requires an extra "push", leading to inflection behaviour. The isomer 22DMB is so bulky that it can be located only at the intersections; there is no inflection for this component for the range of temperatures and pressures studied.

**Pure component permeation selectivities across Silicalite membrane** Further verification of the pure component CBMC simulations given in chapter 2 will now be obtained by examining experimental results on permeation of pure components across a silicalite membrane. Funke et al. [60] have presented data on the ratio of permeation fluxes of (1) n-C<sub>6</sub> and (2) 3MP at 362 K and 405 K, keeping the upstream hydrocarbon pressures at 15 kPa; see Table 3 of their paper. They observed the n-C<sub>6</sub>/3MP permeation selectivities to be 1.3 and 1.9 respectively. Let us first try to rationalise these experimental findings. The permeation flux of component 1, say, is expected to be proportional to the Fick diffusivity,  $D_1$ , inside the zeolite matrix and

the driving force for transport across the membrane,  $\Delta\Theta_1$ , which is the difference between the molecular loadings in the upstream and downstream faces of the membrane. In their membrane experiments the downstream membrane compartment is purged with inert gas, keeping the partial pressures to near zero values. Therefore the driving force  $\Delta\Theta_1$  can be taken to be the loading corresponding to the upstream pressure conditions, i.e.  $\Delta\Theta_1 = \Theta_1$  corresponding to  $p_1$ . The flux of any component is therefore proportional to the diffusivity of that component and its molecular loading at the upstream pressure conditions. The sorption isotherm is therefore an important determinant in the permeation behaviour across a membrane. From the experimental data on the pure component permeations in two separate experiments, the permeation selectivity  $S_p$  can be calculated as follows:

$$S_p = \frac{D_1}{D_2} \frac{\Theta_1}{\Theta_2} \frac{p_2}{p_1} \tag{3.1}$$

In Figure 3.7 (a) the measured values of  $S_p$  are compared with the sorption selectivity S:

$$S = \frac{\Theta_1}{\Theta_2} \frac{p_2}{p_1} \tag{3.2}$$

determined from CBMC simulations. The values of  $S_p$  and S are quite close to one another, suggesting that the ratio of Fick diffusivities  $D_1/D_2$  of the linear and branched isomers, n-C<sub>6</sub> and 3MP, is close to unity. It is noteworthy that the ratio of pure Fick diffusivities measured by Cavalcante and Ruthven [38] for n-C<sub>6</sub> and 3MP is much higher than unity. The precise reasons behind this discrepancy are not known. It appears that to interpret membrane permeation data one must measure the pure component Fick diffusivities using the same membrane and not rely on single crystal or chromatographic studies for this information.

Gump et al. [63] have presented experimental results for the permeation fluxes of pure components n-C<sub>6</sub> and 22DMB across a silicalite membrane at 353 K and at various upstream pressures; see Figure 4 of their paper. We calculated the permeation selectivities  $S_p$  for these experiments and compared them with the sorption selectivities S using the pure component CBMC simulations at 353 K; the comparison between  $S_p$  and S is shown in Figure 3.7 (b). We again note the close agreement between the permeation and sorption selectivities. The values of  $S_p$  are consistently higher than that of S suggesting that the ratio of Fick diffusivities  $D_1/D_2$  of the linear and branched isomers, n-C<sub>6</sub> and 22DMB, is only slightly higher than unity. It is again to be noted that the ratio of pure Fick diffusivities of n-C<sub>6</sub> and 22DMB measured by Boulicaut et al. [81] is a few orders of magnitude higher than unity and the reasons behind this discrepancy remain unclear.

Funke et al. [60] also published experimental results for the permeation fluxes of pure components 3MP and 22DMB across a silicalite membrane at 362 K keeping the upstream hydrocarbon pressure at 12 kPa; see Table 5 of their paper. We calculated the permeation selectivities  $S_p$  for this experiment and compared them with the sorption selectivities S using the pure component CBMC simulations at 362 K; the comparison between  $S_p$  and S is shown in Figure 3.7 (c). Once again we note



Figure 3.7: Comparison of experimental data with CBMC simulations for sorption selectivities based on pure component data.



Figure 3.8: CBMC simulations for 50-50 mixture isotherms for nC<sub>6</sub>-3MP at 362 and 443 K

the close agreement between the permeation and sorption selectivities. The results of Figure 3.7 allow us to conclude that the CBMC simulations can be used with confidence to estimate the pure component permeation selectivities of hexane isomers across a silicalite membrane.

**Sorption of n-hexane - 3-methylpentane mixtures** Let us now consider sorption of a 50-50 mixture of  $n-C_6$  and 3MP at temperatures of 362 K and 443 K. CBMC simulations for the loadings in the mixture as shown in Figures 3.8 (a) and (b) for a range of pressures. It is interesting to note the maximum in the loading of 3MP at about 100 Pa for 362 K and at about 10000 Pa at 443 K. When the pressure is raised above these pressures the loading of 3MP reduces virtually to zero. The  $n-C_6$  molecules fit nicely into both straight and zigzag channels [33] whereas the 3MP molecules are preferentially located at the intersections between the straight channels and the zigzag channels; see Figure 3.2. The  $n-C_6$  have a higher packing efficiency within the silicalite matrix than the 3MP molecules. It is more efficient to obtain higher loading by "replacing" the 3MP with  $n-C_6$ ; this configurational entropy effect is the reason behind the curious maxima in the 3MP loading in the mixture.

Before seeking experimental verification of the curious mixture behaviour, let us try to estimate the mixture loadings from the pure component isotherms using the Ideal Adsorbed Solution theory (IAST) of Myers and Prausnitz [85]. We have chosen the IAST in view of the recent success obtained with the description of mixture isotherms of light alkanes in silicalite [83, 84]. Details on IAST as well as the fitting procedure can be found in ref. [27]. We see in Figures 3.8 (a) and (b) that the IAST predictions are in reasonably good agreement with the CBMC mixture loadings. Some deviations are observed, especially at high loadings. These deviations are caused by mixture non-ideality effects. Funke et al. [60] measured the permeation selectivities for 50-50 mixtures of  $n-C_6$  and 3MP at various temperatures, keeping the upstream hydrocarbons pressure at 15 kPa; see Table 3 of their paper. What is remarkable is that the permeation selectivity for a 50-50 mixture  $S_p = 24$  whereas  $S_p = 1.3$  for the pure components. This high mixture selectivity can be explained by examination of Figure 3.8 (a), where the upstream pressure (15 kPa) condition of the Funke experiment is indicated by a vertical line. The upstream pressure corresponds to a situation well beyond the pressure at which the 3MP loading exhibits a maximum and the sorption selectivity is very high. In another experiment at 443 K, the upstream pressure of 15 kPa corresponds closely to the pressure at which the loading of 3MP is at its maximum and therefore the selectivity of  $n-C_6$  is at its lowest. The CBMC simulations also show that in order to obtain high selectivities at 443 K, the upstream pressure should be maintained at 1000 kPa. Since at such high pressures, the hydrocarbon mixture would be in the liquid phase, one technological solution would be to operate in the pervaporation mode (upstream compartment in the liquid phase; downstream compartment in the vapour phase). Matsufuji et al. [86] have shown that high selectivities for the separation of hexane isomers can be obtained by operating in the pervaporation mode, underlining these arguments. From the mixture isotherms presented in Figure 3.8 (a) and (b) it becomes clear that configurational entropy effects would manifest only at higher pressures, i.e. at high mixture loadings. In order to stress this point, we have calculated the sorption selectivity, S, as a function of the total mixture loading; the results are presented in Figures 3.9 (a) and (b). The sorption selectivity increases sharply beyond a total loading of 4 molecules per unit cell, corresponding to the situation in which all the intersections are occupied. The experimental permeation selectivities  $S_p$ , measured by Funke et al. [60], are compared with the sorption selectivities S in Figure 3.9 (c) for a range of temperature conditions keeping the pressure at 15 kPa. The close agreement between the two sets of results confirm the configurational entropy effects are the reasons behind the high selectivities observed at lower temperatures. Such effects diminish with increasing temperatures, when the pressure is maintained constant at 15 kPa.

**n-hexane - 2,2dimethylbutane mixtures** CBMC simulations carried out for a 50-50 mixture of (1) n-C<sub>6</sub> and (2) 22DMB at 398 K, also show that the double-branched is virtually excluded at higher pressures due to configurational entropy effects; see Figure 3.10 (a). From Figure 3.10 (b) we see that the sorption selectivity increases dramatically beyond a total mixture loading of 4 molecules per unit cell. Gump et al. [63] have reported the permeation fluxes of 50-50 mixtures of n-C<sub>6</sub> and 22DMB across a silicalite membrane at 398 K for various upstream hydrocarbon pressures; see Figures 5 and 6 of their paper. Since the flux of any component is proportional to the loading at the upstream face, we would expect the flux of 22DMB to go through a maximum as the upstream compartment pressure is increased, in steps, from say 100 Pa to 100 kPa. This is precisely what Gump et al. [63] have observed in their experiments. The experimental fluxes of 22DMB are compared in Figure 3.10 (c) with the 22DMB loadings obtained from CBMC simulations. It is heartening to note that the experimentally observed maximum flux of 22DMB is obtained at the same pressure at which the 22DMB exhibits a maximum in its loading.

Gump et al. [63] have also reported the permeation fluxes of mixtures of  $n-C_6$  and 22DMB across a silicalite membrane at 373 K for various mixture compositions;



**Figure 3.9:** Sorption and permeation selectivities for a 50-50 mixture of  $nC_6$ -3MP at 362 and 443 K



**Figure 3.10:** (a) CBMC simulations of a 50-50 mixture isotherm for  $nC_6$ -22DMB at 398 K. (b) Sorption selectivity from CBMC simulations. (c) Comparison of loading of 22DMB with fluxes measured by Gump et al. [63]

see Figures 1 and 2 of their paper. The most intriguing results are the permeation fluxes for 22DMB which show a maximum for a set of vapour compositions  $y_1 = 0.2, 0.3$  and 0.4; see Figure 2 of their paper. In order to understand these permeation results, the molecular loadings of n-C<sub>6</sub> and 22DMB were determined for the same set of conditions as in the experiments. Our CBMC simulation results for 22DMB loadings are compared with the 22DMB fluxes in Figures 3.11 (a-c). For  $y_1 = 0.2, 0.3$  and 0.4 the 22DMB loading exhibits a maximum at the same upstream pressure at which the flux maximum is observed. For all three mixtures, the sorption selectivities are shown in Figure 3.12; we see the sharp increase in the selectivity for total mixture loadings in excess of 4 molecules per unit cell.

From the results presented in Figures 3.9, 3.10 and 3.11 we confirm that configurational entropy effects cause the exclusion of the branched isomer from the silicalite structure. Our explanation of the membrane permeation experiments is essentially different from that proposed by Funke et al. [60] and Gump et al. [63], who consider the n-hexane to effectively "block" the permeation of branched isomers. These authors do not offer an explanation of their membrane permeation experimental results in terms of the entropy effects explained here.

For a more extensive analysis with mixtures in the 5-7 carbon range the reader is referred to ref. [27].

## 3.4 Conclusions

We have examined the sorption characteristics of various mixtures of hexane isomers. The following major conclusions can be drawn: (1) CBMC simulations provide a powerful technique for determining the pure component and mixture isotherms of alkanes. The simulated pure component isotherms are in good agreement with experiment. There are no published experimental mixture isotherms and therefore CBMC simulations come into their own. (2) For mixtures of linear and branched alkanes with the same number of carbon atoms, the sorption selectivity increases in favour of the isomer with the highest packing efficiency. This is a configurational entropy effect which is so strong that the branched alkanes are virtually excluded from the silicalite matrix and high separation factors are achievable. In AFI the selectivity at high loading is towards 22DMB. (3) The mixture isotherm characteristics are captured in essence by the IAS theory. (4) A characteristic feature of the configurational entropy effects for alkanes isomers in MFI is that for mixture loadings above 4, the loading of the branched alkane decreases when the system pressure increases. This has implications when a mixture of linear and branched alkanes permeate across a silicalite membrane. At high mixture loadings, the flux of the branched alkane must decrease while the upstream partial pressure increases; this curious behaviour has indeed been observed experimentally by Gump et al. [63]. Their experimental results can be rationalised on the basis of our CBMC mixture simulations.



Total hydrocarbons pressure/[Pa]

**Figure 3.11:** Comparison of CBMC simulations of loading with experimentally determined fluxes of 22DMB for mixtures of  $nC_6$ -22DMB at 373 K with various vapor phase compositions. Experimental data are from Gump et al. [63]



**Figure 3.12:** CBMC simulations of sorption selectivity for mixtures of nC<sub>6</sub>-22DMB at 373 K with various vapor phase compositions.

# $\displaystyle IV$ Shape selectivity in alkane conversion, studied in the Henry regime $^1$

In the next two chapters we will use the methods described in chapters 1 and 2 to elucidate a few examples of the sometimes peculiar shape selective processes found in zeolites. In this chapter we focus on the shape selectivity imposed by a zeolite framework on hydrocarbon conversions which take place at very low loading. This means that the adsorbed hydrocarbons will only "feel" the presence of the zeolite wall, but not each other's presence. We will use three test cases to outline the line of reasoning, introduced in the introduction, of linking shape selectivity to adsorption thermodynamics: (1) The use of TON-, MTT- and AEL-type zeolites in the dewaxing of long n-paraffins. (2) The difference in cracking performance between two similar zeolites MFI and MEL. (3) The effect of commensurability of 2,x-dimethylpentadecanes on the diffusion and conversion in TON.

Before we look at the three test cases, it is instructive to briefly summarize the five types of shape selectivity we can distinguish at very low loading [3,88–93] (see Figure 4.1 for an illustration):

- **Transition state shape selectivity** is the result of restrictions to the spacial configuration of transition states and reaction intermediates imposed by the zeolite framework, i.e. the predominant reactions have transition states and reaction intermediates of relatively low Gibbs free energy of formation.
- **Reactant shape selectivity** takes place when the zeolite acts as a molecular sieve, excluding reactants which are too bulky for the pore system, i.e. zeolites preferentially consume molecules that combine a low Gibbs free energy of adsorption with a low Gibbs free energy barrier to diffusion.
- **Product shape selectivity** is the result of differences in desorption rate between various reaction products due to differences in diffusivity and adsorption strength, i.e. zeolites preferentially yield molecules that combine a high Gibbs free energy of adsorption with a low Gibbs free energy barrier to diffusion.
- **Reaction intermediate shape selectivity** occurs when some reaction intermediates have a greater influence on the final product distribution than others. i.e.

<sup>&</sup>lt;sup>1</sup>This chapter is based on refs. [87–89]



**Figure 4.1:** Shape selectivity concepts [3,88–93]: Reactant shape selectivity (RS), Product shape selectivity (PS), Transition state shape selectivity (TS), Reaction intermediate shape selectivity (RI), and Partial adsorption selectivity (PA).

zeolites preferentially yield products which are formed through reaction intermediates that combine a low Gibbs free energy of adsorption (and formation in the adsobed phase) with a high Gibbs free energy barrier to diffusion.

• **Partial adsorption selectivity** occurs when a reactant is only able to partially enter the pore. Consequently all reactions, like isomerizations and scissions, take place at the pore-mouth.

## 4.1 Alkane hydroconversion on TON-, MTT- and AEL-type zeolites

A recent example of the use of zeolites is the catalytic upgrading of lubricating oils [94]. Noble metal loaded AEL-type silicoaluminophosphate zeolites selectively absorb the wax-like, long-chain normal alkanes from an oil feedstock and hydroconvert them selectively into branched alkanes [94–96]. Catalysts based on TON- [97–100] and MTT-type [94,97,100–102] zeolites combine a strong affinity for long-chain, normal alkanes with a significantly higher selectivity for hydroisomerization than for hydrocracking [94–102].

Examination of the product slates reveals that when hydroisomerising normal alkanes, TON-, MTT- and AEL-type zeolites preferentially introduce the first methyl group at a terminal position [96–100, 103, 104]. Subsequent methyl groups are introduced at positions two or more methylene (viz. -CH<sub>2</sub>-) groups removed from the ones already present [93, 96–100, 105]. Since alkanes with methyl groups separated by fewer than two methylene groups are more susceptible to hydrocracking [99, 103],

suppressing their formation automatically reduces the extent of hydrocracking. The selective adsorption and selective hydroconversion of the long-chain normal alkanes from a complex feedstock are characteristic of the 0.4-0.6 nm channel size [106] of the AEL-, TON- and MTT-type zeolites. The selective adsorption clearly constitutes an example of reactant shape selectivity (RS, Figure 4.1) [90, 91, 94]. Less clear is how the preferential hydroisomerization relates to the shape selectivity imparted by the tubular one-dimensional AEL-, TON- and MTT-type channels [106].

Current theories attribute the peculiar hydroisomerization pattern of AEL-, TON-, and MTT-type zeolites to either (1) pore mouth catalysis (PM) [93, 99, 104, 105], (2) transition state shape selectivity (TS) [98, 100, 103, 107], or (3) product shape selectivity (PS) [98, 108]. The first theory postulates that the terminal branching occurs entirely at the pore mouths, because the required transition state does not fit inside a TON-type channel [93,99,104,105]. This theory has not been expanded to cover MTTand AEL-type zeolites. Since this model further postulates that none of the branched alkanes [104, 109] can fully enter the TON-type pores, it has to postulate that subsequent hydroisomerization reactions (to form di- and multi-branched alkanes) occur at the pore mouths or at the external surface [93,99,105]. The second theory suggests that the transition state required for terminal methyl groups is better able to fit inside the these alkanes AEL-, TON- and MTT-type channels than the transition state for alkanes with internal methyl groups [98, 100, 107]. Therefore, these channels would energetically favor the formation of the former. The third theory suggests a higher desorption rate for alkanes with terminal methyl groups than for alkanes with internal methyl groups [98, 108]. The former therefore have shorter residence times and are less prone to consecutive reactions (PS) [98, 108].

To understand which of the assumptions underlying these theories is most accurate requires detailed information on the adsorption of the alkanes inside the zeolitic pores. Information on a molecular level can be obtained by complementing experimental adsorption data [109] with molecular simulations. This section compares the simulated sorption data with experimental sorption data available in the literature [109]. The results of this comparison are then used to explain the differences between n-heptane (n-C<sub>7</sub>) hydroconversion on TON-, MTT-, AEL-type zeolites and FAU- or BEA-type zeolites. FAU- and BEA-type zeolites were chosen as a base case as their pores are too large to exert significant shape selectivity [16, 110–113]. Enough is known about the influence of the chain length on the hydroisomerization selectivity of n-alkanes [12, 104] to allow translation of the results for n-C<sub>7</sub> to the longer-chain alkanes that are more commonly described in the literature [97–100, 102–104, 104, 105, 107, 108].

## 4.1.1 Experimental methods

The catalyst based on TON-, MTT-, AEL-, and FAU-type zeolites were prepared and analyzed according to the procedure described in ref. [87]. The n-heptane hydrocracking experiments are also described in ref. [87].

	Measured	Calculated	Calculated	Calculated
Name	TON	TON	MTT	AEL
Pentane	-62.1	-62.0	-55.1	-60.5
2MeBut	-50.4	-59.8	-47.9	-57.4
Hexane	-75.0	-74.5	-67.1	-70.6
2MePen	-62.4	-69.9	-54.3	-71.5
3MePen	-61.7	-69.9	-54.1	-63.6
22diMeBut	-38.2	11.8	-45.9	-10.1
23diMeBut	-52.2	-60.6	-51.5	-61.1
Heptane	-87.9	-85.9	-76.3	-81.9
2MeHex	-75.4	-84.6	-69.7	-81.4
3MeHex	-69.8	-81.4	-66.2	-78.5
23diMePen	-60.2	-73.8	-46.0	-71.6
33diMePen	-	6.3	-55.5	-15.2

**Table 4.1:** Measured [109] and calculated heats of adsorption (kJ/mol), *T*=573 K.

### 4.1.2 Results and discussion

To establish which alkanes are able to fit inside the pores of AEL-, TON, and MTTtype zeolites, we compare the adsorption enthalpies and Henry coefficients calculated by the CBMC technique with those measured [109] on a TON-type zeolite (Tables 4.1 and 4.2). The correlation between calculated and measured Henry coefficients of all the alkanes is excellent (Figure 4.2, correlation coefficient R2=0.995), and so is the correlation between the calculated and measured adsorption enthalpies of the linear alkanes (Figure 4.3, R2=0.995). The adsorption enthalpies calculated for the branched alkanes are consistently 7 kJ/mol lower than the measured ones (Figure 4.3, R2=0.95) suggesting a systematic error in the force field. This could be the result of optimizing the force field for adsorption in a MFI-type silicate framework, and not a TON-type silicate. Moreover, the simulations assume a TON-type pure silicate whereas the experimental TON-type sample is a zeolite containing protons and framework aluminum. Despite these differences, the simulations are in good agreement with the experimental data.

The CBMC technique simulates adsorption inside perfect, infinitely long, TONtype channels. Therefore the good agreement between the experimental and simulated adsorption data for normal and mono-branched alkanes implies that crystal imperfections or crystal boundaries did not significantly affect the experimental [109] data, and that the n-C<sub>7</sub> and mono-branched heptanes (i-C<sub>7</sub>) are fully adsorbed inside the TON-type channels. The di-branched heptanes (henceforth referred to as ii-C<sub>7</sub>) merit a more detailed evaluation.

The calculated adsorption enthalpies for di-branched alkanes with *geminal* methyl groups (such as 3,3-dimethylpentane and 2,2-dimethylbutane) are positive (Table 4.1) and the Henry coefficients approach zero mmol/kgPa (Table 4.2), suggesting that the TON-type channels do not permit access to this type of alkanes. The experimentally





**Figure 4.2:** Comparison of measured and calculated Henry coefficients ( $\mu$ mol/kg Pa), *T*=573 K: data ( $\blacklozenge$ ), and correlation (-).

**Figure 4.3:** Comparison of measured and calculated heats of adsorption (kJ/mol): ▲ linear alkanes, • branched alkanes.

	Measured	Calculated	Calculated	Calculated
Name	TON	TON	MTT	AEL
Pentane	$1.32 \times 10^0$	$6.45\times10^{-1}$	$3.92\times 10^{-2}$	$4.14\times10^{-1}$
2MeBut	$3.23 \times 10^{-1}$	$1.23 \times 10^{-1}$	$3.37 \times 10^{-3}$	$1.07 \times 10^{-1}$
Hexane	$2.59 \times 10^0$	$1.43 \times 10^0$	$7.84\times10^{-2}$	$6.80 \times 10^{-1}$
2MePen	$5.42 \times 10^{-1}$	$2.28\times10^{-1}$	$3.88\times10^{-3}$	$4.71 \times 10^{-1}$
3MePen	$4.42\times10^{-1}$	$1.76 \times 10^{-1}$	$6.93\times10^{-4}$	$6.39\times10^{-2}$
22diMeBut	$1.30 \times 10^{-1}$	$1.80 \times 10^{-9}$	$1.52\times 10^{-4}$	$1.16 \times 10^{-7}$
23diMeBut	$2.39\times10^{-1}$	$7.42\times10^{-3}$	$2.01\times 10^{-4}$	$9.86\times10^{-3}$
Heptane	$4.66  imes 10^0$	$2.81 \times 10^0$	$7.21\times 10^{-2}$	$9.84  imes 10^{-1}$
2MeHex	$1.13  imes 10^0$	$6.74\times10^{-1}$	$1.58\times 10^{-2}$	$8.13\times10^{-1}$
3MeHex	$8.71\times10^{-1}$	$3.42 \times 10^{-1}$	$1.32 \times 10^{-3}$	$2.11\times 10^{-1}$
23diMePen	$4.19\times10^{-1}$	$1.54\times10^{-2}$	$1.22\times10^{-5}$	$1.83 \times 10^{-2}$
33diMePen	_	$5.98\times10^{-0}$	$3.75\times10^{-5}$	$4.51\times 10^{-8}$

Table 4.2: Measured [109] and calculated Henry coefficients (µmol/kg Pa), T=573 K.

determined Henry coefficient of 0.13 mmol/kgPa for 2,2-dimethylbutane (Table 4.1) can be explained as resulting from adsorption outside the pores (at sample imperfections such as pore mouths and intercrystalline voids) [109].

The calculated Henry coefficients for di-branched alkanes with *vicinal* methyl groups (such as 2,3-dimethylpentane and 2,3-dimethylbutane), are slightly below the experimental values (Table 4.2). The calculated adsorption enthalpies compare well with the experimentally determined enthalpies of adsorption, and are not as prohibitively high as those of alkanes with *geminal* methyl groups (Table 4.1). It is tempting to conclude that the size of ii- $C_7$  molecules with *vicinal* methyl groups is at the limit of what can fit inside the TON-type pores. The same holds true for the slightly smaller ii- $C_7$  with methyl groups separated by one CH<sub>2</sub>- group (quasi-*vicinal* methyl groups). The simulations, which employ a rigid framework, do not allow us to draw unambiguous conclusions about the adsorption of molecules whose size approaches that of the pore diameter. Additional conclusions about the constraints imposed by TON-, MTT- and AEL-type channels on these types of ii- $C_7$  molecules can be derived from the results of the catalytic n- $C_7$  hydroconversion tests (see below).

In order to discuss the peculiarities of the shape selective  $n-C_7$  hydroisomerization, it is useful to first address what happens in the absence of shape selectivity, using the non-selective  $n-C_7$  hydroconversion on Pt-loaded FAU- and BEA-type zeolites as an example. Under the experimental conditions, the FAU- and BEA-type zeolites exhibit virtually identical selectivity (Table 4.3). The following model can be used to describe the hydroisomerization of  $n-C_7$  into  $i-C_7$ ,  $ii-C_7$ , and the subsequent hydrocracking of  $ii-C_7$  to yield iso-butane ( $i-C_4$ ) and propane ( $C_3$ ) [12, 16, 110–113] (Figure 4.4):

$$n - C_7 \rightleftharpoons i - C_7 \rightleftharpoons ii - C_7 \to i - C_4 + C_3 \tag{4.1}$$

Since the yield of 2,2,3-trimethylbutane remains below 1.5 wt-%, is not included in the discussion. As observed elsewhere [16], FAU- and BEA-type zeolites yield the two i- $C_7$  molecules (2- and 3-methylhexane) at thermodynamic equilibrium (Figure 4.4A). The kinetically favored 2,3-dimethylpentane [111] and thermodynamically favored 2,4-dimethylpentane [111] dominate the ii- $C_7$  yield (Figure 4.4B). The approximately equal yield of i- $C_4$  and of  $C_3$  (Figure 4.4C) indicates [111] that FAU- and BEA-type zeolites predominantly hydrocrack ii- $C_7$  as opposed to i- $C_7$ . The methane and ethane yields of the FAU and BEA-type zeolites remain below 0.1 wt-% (at 98% conversion) indicating that the Pt phase is sufficiently active to establish an equilibrium between the adsorbed alkanes and the alkenes and that Pt-catalyzed cracking [110–112] and hydroisomerization [114,115] are negligible. The catalysts based on TON-, MTT- and AEL-type zeolites have a slightly higher Pt-catalyzed hydroconversion (combined methane and ethane yield 4 wt-% at 98% conversion).

The n-C<sub>7</sub> hydroconversion selectivity of TON- and MTT-type zeolites (Figure 4.5) is markedly different from that of FAU- or BEA-type zeolites (Figure 4.4). Notwithstanding the difference in pore shape [106,116] and sorption properties (Tables 4.1,4.2) between the TON- and MTT-type zeolites, their n-C<sub>7</sub> hydroconversion selectivity is comparable (Table 4.3). Both yield a ratio of terminal i-C<sub>7</sub> (viz. 2-methylhexane) to internal i-C<sub>7</sub> (viz. 3-methylhexane) in excess of thermodynamic equilibrium (Figure

structure	max diameter	min diameter	$T_{40\%}$	max i-C7	max ii-C7	Eact
type	(nm)	(nm)	(K)	(wt-%)	(wt-%)	(kJ/mol)
FAU	0.74	0.74	510	50.1	24.4	134
BEA	0.76	0.55	492	51.7	21.7	138
TON	0.55	0.44	525	66.2	5.7	141
MTT	0.52	0.45	537	66.0	5.0	140
MTT	0.52	0.45	521	66.2	4.7	144
AEL	0.63	0.39	578	62.2	14.7	118

**Table 4.3:** Pore dimensions, temperature required for 40% n-C<sub>7</sub> hydroconversion ( $T_{40\%}$  (K)), maximum i-C<sub>7</sub>, and ii-C<sub>7</sub> yield (wt-%), and activation energy  $E_{act}$  (kJ/mol).



**Figure 4.4:** Figure 4.4A: i-C<sub>7</sub> yield pattern on FAU- or BEA-type zeolite: • 2-methylhexane, • 3-methylhexane Figure 4.4B: ii-C<sub>7</sub> yield pattern on FAU- or BEA-type zeolite: • 2,4dimethylpentane, • 2,3- dimethylpentane, **I** 3,3-dimethylpentane, **I** 2,2-dimethylpentane. Figure 4.4C: n-C<sub>7</sub> hydrocracking pattern on FAU- or BEA-type zeolite:  $\triangle$  propane, **I** isobutane, • n-butane Figure 4.4D: n-C<sub>7</sub> hydroconversion pattern on FAU- or BEA-type zeolite: • i-C<sub>7</sub>, **I** ii-C<sub>7</sub>, **I** c<sub>4</sub> + C<sub>3</sub>.



**Figure 4.5:** Figure 4.5A: i-C<sub>7</sub> yield pattern on TON- or MTT-type zeolite: • 2-methylhexane, • 3-methylhexane Figure 4.5B: ii-C<sub>7</sub> yield pattern on TON- or MTT-type zeolite: • 2,4dimethylpentane, • 2,3- dimethylpentane,  $\blacksquare$  3,3-dimethylpentane,  $\square$  2,2-dimethylpentane. Figure 4.5C: n-C<sub>7</sub> hydrocracking pattern on TON- or MTT-type zeolite:  $\triangle$  propane,  $\blacksquare$  isobutane, • n-butane Figure 4.5D: n-C<sub>7</sub> hydroconversion pattern on TON- or MTT-type zeolite: • i-C<sub>7</sub>,  $\blacksquare$  ii-C<sub>7</sub>,  $\land$  C<sub>4</sub> + C<sub>3</sub>.

4.5A), whereas FAU- and BEA-type zeolites yield i- $C_7$  at equilibrium. As discussed above, current theories explain this high selectivity for terminal methyl groups in terms of either (1) pore mouth catalysis (PM), (2) transition state selectivity (TS), or (3) product selectivity (PS).

Pore mouth catalysis (PM) was born when molecular graphics calculations suggested that neither the transition state, nor a branched alkane, would fit inside the TON-type pores [104]. Therefore it was postulated that hydroisomerization favors the formation of a terminal methyl group because hydroisomerization occurs exclusively at the supposedly enlarged [93, 99] TON-type pore mouths. Recent evaluations [117, 118] of the transition state for alkane hydroisomerization show that size of the transition state in the original molecular graphics calculations [104, 119] was overestimated. According to this recent assessment [117, 118], the transition state for forming i-C<sub>7</sub> (a corner-protonated 1-methyl, 2-propyl- or a 1,2-diethylcyclopropyl cation [111], see Figure 4.6) is smaller than i-C<sub>7</sub>. Comparing experimental data with CBMC calculations, we have established that i-C<sub>7</sub> fits inside the TON-type pores. Since the transition state for i-C<sub>7</sub> is smaller than its i-C<sub>7</sub> product, it too should fit



Figure 4.6: Relevant reactants, transition states and products of n-C<sub>7</sub> hydroconversion.

snugly inside the TON-type channels, and there is no reason for their preferential formation at the pore mouths. Thus the molecular graphics basis for postulating pore mouth catalysis appears not to have withstood the test of time. This leaves transition state (TS) and product selectivity (PS) as viable explanations for the enhanced selectivity for terminal methyl groups.

If the i- $C_7$  product distribution were dependent on the transition state for the hydroisomerization of  $n-C_7$  into  $i-C_7$ , we would expect FAU- and BEA-type zeolites to yield predominantly the kinetically favored internal methyl groups (Figure 4.6). This is not the case (Figure 4.4A), because intra-molecular methyl-shifts rapidly bring the i-C<sub>7</sub> molecules with terminal and with internal methyl groups to thermodynamic equilibrium [111]. Since methyl-shifts appear to nullify the effect of the transition states in FAU- and BEA-type zeolites, transition state selectivity is unlikely to be the main explanation for the shape selective production of alkanes with terminal methyl groups by the TON- and MTT-type pores. Nonetheless, it cannot be ruled out entirely [100,107] without a more careful study similar to that carried out for MFI-type zeolites [103]. A more plausible explanation is that these pores contain equal amounts of alkanes with terminal and with internal methyl groups (the equilibrium distribution), and selectively release more of the former as they diffuse faster out of the pores (PS). Indeed, for several zeolites, the ratio of the selectivity for alkanes with a terminal methyl group to that for alkanes with an internal methyl group appears to correlate quite well with the ratio of the respective diffusion rate of these molecules out of the zeolite pores [108].

Not only the i- $C_7$  product slate, but also the ii- $C_7$  product slate of TON- and MTT-type zeolites is markedly different from that of FAU- and BEA-type zeolites

(cf. Figures 4.4B, 4.5B). The TON- and MTT-type zeolites yield no alkanes with geminal methyl groups and only few with (quasi-) vicinal methyl groups, preferentially yielding 2,4-dimethylpentane (Figure 4.5B). This absence of *geminal* methyl groups confirms that the TON- and MTT-type channels exclude them. Pore mouth catalysis (PM) postulates that the TON-type structure absorbs monomethylalkanes at the outer crystal surface by pinning them down by a methyl group at a pore mouth (key-lock mechanism [93,99,105]). Subsequent hydroisomerization occurs at the active sites in a neighboring pore mouth, and the position of the subsequent branches is governed by the position of the neighboring pore mouths [93, 99, 105]. This model cannot explain the preferential formation of 2,4-dimethylpentane, because the i- $C_7$  chain is too short to bridge the space between neighboring pore mouths. As demonstrated above, the i- $C_7$  is able to enter the TON-type pores. Given its high adsorption enthalpy (Table 4.1) it will enter the pores and will not linger at or near the outer crystal surface. This leaves transition state (TS) and product selectivity (PS) as the only feasible options for explaining the shape selective formation of 2,4-dimethylpentane inside the TON- and MTT-type pores.

The size of the transition state for forming i-C<sub>7</sub> approaches that of i-C<sub>7</sub> [117, 118]. By the same token we expect the size of the (corner-protonated) trialkyl cyclopropyl transition state for forming *geminal* methyl groups (Figure 4.6) to approach the size of their products. Since the TON- and MTT-type pores exclude the products, they can reasonably be expected to exclude the transition states. The resulting inhibition leaves only the dialkyl cyclopropyl cation transition state for forming dimethylalkanes (Figure 4.6). Having only one out of three transition states available for forming ii-C<sub>7</sub> (Figure 4.6) would explain the comparatively low yield of ii-C<sub>7</sub> (cf. Figures 4.4B, 4.5B) (TS). When the dialkyl cyclopropyl cation transition state is the only route towards dimethylalkanes, it will initially yield equal amounts of 2,3- and 2,4-dimethylpentane (Figure 4.6). The enhanced yield of the latter suggests that these ii-C<sub>7</sub> molecules reside long enough inside the TON- and MTT-type channels for methyl shifts to generate predominantly the thermodynamically favored, faster diffusing 2,4-dimethylpentane [111] (PS).

The shape selectivity of the TON- and MTT-type zeolites is also evident in their hydrocracking product slate (Figure 4.5C). Whilst FAU- or BEA-type zeolites predominantly yield  $C_3$  and i- $C_4$  (Figure 4.4C), the TON- and MTT-type product slates are complemented with significant quantities of n-butane (Figure 4.5C). The presence of n-butane implies that these zeolites impede i- $C_7$  hydroisomerization to such an extent that the energetically less favorable i- $C_7$  hydrocracking becomes significant [111]. The postulated inhibition of the formation of trialkyl cyclopropyl transition states impedes i- $C_7$  hydroisomerization, for it would require 3-methylhexane to methyl-shift into 2-methylhexane before it is able to hydroisomerize (Figure 4.6). In addition, it would leave 2-methylhexane with access to only one instead of two transition states for hydroisomerization (Figure 4.6). The remaining transition state for i- $C_7$  hydroisomerization is still quite bulky, for it contains a methyl group adjacent to the cyclopropyl cation (Figure 4.6). We can easily envisage that the restricted space available inside the TON- and MTT-type channels increases the formation energy of such a bulky transition state to the extent that it approaches the activation energy for i- $C_7$  hydrocracking (TS). This would explain why an energetically unfavorable reaction such as  $i-C_7$  hydrocracking occurs concomitantly with  $i-C_7$  hydroisomerization.

Having shown how the transition state and product shape selectivity affect the individual product slates we are now in a position to address the overall n-C<sub>7</sub> hydroisomerization reaction in the TON- and MTT-type zeolites (Figure 4.5D). Compared with FAU- and BEA-type zeolites (Figure 4.4D), the TON- and MTT-type zeolites yield more i-C<sub>7</sub>, less ii-C<sub>7</sub>, and start hydrocracking at a lower hydroconversion level (Figure 4.5D). The enhanced i-C<sub>7</sub> selectivity and reduced ii-C<sub>7</sub> selectivity can be explained by the impediment of the consecutive hydroisomerization of i-C<sub>7</sub> into ii-C<sub>7</sub> (TS). The onset of hydrocracking at lower conversion can be attributed to branched alkanes being constrained inside the tubular TON- and MTT-type channels. The increased intracrystalline residence time (as compared to FAU- or BEA-type zeolites) increases the chance of these molecules being hydrocracked (PS).

As may be predicted based on its intermediate pore size (Table 4.3) [106], the n- $C_7$  hydroconversion selectivity of the AEL-type silicoaluminophosphate lies somewhere in between that of the FAU- or BEA-type zeolites and the TON- or MTT-type zeolites. As with FAU- and BEA-type zeolites, the AEL-type zeolite yields a product slate that is only marginally enhanced in i- $C_7$  molecules with terminal methyl groups (Figure 4.7A), contains alkanes with *geminal* methyl groups, and is dominated by the kinetically favored 2,3-dimethylpentane (Figure 4.7B). Like TON- and MTT-type zeolites, the AEL-type zeolite has a high i- $C_7$  selectivity (Figure 4.7D), a low ii- $C_7$  selectivity (particularly for ii- $C_7$  molecules with *geminal* methyl groups, Figure 4.7B), and hydrocracks i- $C_7$  (Figure 4.7C) at relatively low conversion (Figure 4.7D).

The concepts for explaining the hydroconversion of n-C7 on TON-, MTT- and AEL-type zeolites can also be used to explain the hydroconversion of longer-chain alkanes like n- $C_{12}$  [97], n- $C_{16}$  [96], and n- $C_{17}$  [99]. When converting longer-chain alkanes, these particular zeolites enhance not only the selectivity for mono-branched but also that for di-branched alkanes, and they suppress hydrocracking [93,96–100, 102-104, 107]. The methyl groups in the di-branched alkanes are at least 3 methylene groups apart, preferably even further [93, 96, 97, 99, 102, 105]. Analogous to i- $C_7$ , transition state selectivity would explain the inhibition of *geminal* methyl groups and the absence of (quasi-) vicinal methyl groups. The selectivity for the individual non-inhibited dimethylalkanes will be dominated by their relative diffusion rate (PS). Unlike i-C<sub>7</sub>, the initial methyl group need not affect the consecutive hydroisomerization as long as the second methyl group is introduced far away enough (TS). In the absence of *geminal* or quasi-vicinal methyl groups hydrocracking is more difficult than hydroisomerization [99, 103] (TS), so that both primary and consecutive hydroisomerization can continue until very high n-alkane conversions are reached [93, 96, 97, 99, 105]. Thus, we can explain the phenomena normally used to illustrate pore mouth catalysis concepts [93,99,105] by traditional shape selectivity concepts.

Finally, the activation energy of a reaction can be used to assess whether the complete pore or only the pore mouth is involved in alkane hydroconversion. If the reaction is diffusion limited, the n-alkane hydroconversion will be limited to the pore mouth. Diffusion limitations will lower the apparent activation energy for  $n-C_7$  hydroconversion when the prerequisites for a diffusional increase in apparent activa-



**Figure 4.7:** Figure 4.7A: i-C<sub>7</sub> yield pattern on AEL-type zeolite: • 2-methylhexane, • 3methylhexane Figure 4.7B: ii-C<sub>7</sub> yield pattern on AEL-type zeolite: • 2,4-dimethylpentane, • 2,3-dimethylpentane,  $\blacksquare$  3,3-dimethylpentane,  $\square$  2,2-dimethylpentane. Figure 4.7C: n-C<sub>7</sub> hydrocracking pattern on AEL-type zeolite:  $\triangle$  propane,  $\blacksquare$  iso-butane, • n-butane Figure 4.7D: n-C<sub>7</sub> hydroconversion pattern on AEL-type zeolite: • i-C<sub>7</sub>,  $\blacksquare$  ii-C<sub>7</sub>,  $\blacktriangle$  C<sub>4</sub> + C<sub>3</sub>

tion energy are not met [120–122], as is the case with TON-, MTT- and AEL-type zeolites. We find that the apparent activation energies for the FAU-, BEA-, TON-, MTT-type zeolites are comparable (Table 4.3, estimated systematic error  $\pm 3$  kJ/mol) and approach the true activation energy for hydroisomerization [120, 123, 124]. This indicates that there are no diffusion limitations and therefore all of the zeolite acid sites are able to contribute to the n-C<sub>7</sub> hydroconversion [120, 123, 124], leaving little room for speculation that the n-C<sub>7</sub> hydroconversion in the TON- or MTT-type zeolites occurs predominantly at or near the pore mouth. The apparent activation energy of the AEL-type silicoaluminophosphate is lower than that of the zeolites (Table 4.3), indicating either a lower acid site coverage (due to its higher operation temperature) (Table 4.3) or the onset of diffusion limitations [120, 122]. Determining which is the case would require determining the acid site coverage.

# 4.2 Differences between MFI- and MEL-Type Zeolites in Alkane Hydrocracking

Catalysts based on MFI-type zeolites are widely used in many areas of the oil and petrochemical industries, because of their ability to catalyze reactions shape selectively [125]. They are used in the catalytic upgrading of fuel oil, because they selectively adsorb and hydrocrack wax-like, long-chain normal alkanes into smaller, shorter-chain products [96, 125–127]. Notwithstanding the proven track record of MFI-type zeolites in fuel oil upgrading, a catalyst of comparable activity, but with a higher selectivity for hydroisomerization than for hydrocracking would be desirable as it would yield more valuable fuel oil and less gas.

MEL- and MFI-type zeolites are comparable in terms of activity [103, 128–132]. This is probably related to the similarity of the framework density and the pore size of these structures [2]. Despite these similarities, some studies have suggested that MEL-type zeolites hydroisomerize more alkanes than MFI-type zeolites, at any given alkane hydroconversion level [128–130]. This intrinsic high hydroisomerization selectivity was first postulated based on studies using n-decane ( $n-C_{10}$ ) as a model feed [128], refuted based on studies using n-heptane ( $n-C_7$ ) as a feed [131], and then corroborated by studies using complex feed stocks [129, 130]. It is not clear how the differences in structure between MFI- and MEL-type zeolites translate to the differences in catalytic behavior [131].

Both MFI- and MEL-type zeolites have three-dimensional 0.55 nm channels. The MFI topology consists of intersecting straight and sinusoidal channels, whereas the MEL topology has only straight channels. Consequently, the structure and size of the single MFI-type channel intersection is significantly different from the two distinct MEL-type intersections (Figure 4.8) [2, 132].

Before the advent of molecular simulations, relating the differences between the MFI- and MEL-type zeolite structures to differences in shape selectivity was hindered by a lack of microscopic information on the adsorption and diffusion inside these zeolite structures [126,132].

Here we show how the thermodynamic data obtained by molecular simulations can shed some light on the differences in alkane hydroconversion between MFI- and MEL-type zeolites. As the thermodynamic adsorption data relate to the shape selective properties that are intrinsic to a zeolite structure, we develop a criterion to identify catalytic data that are unimpaired by mass transport or hydrogenation rate limitations. A subsequent scrutiny of the published n-C<sub>7</sub> [131,133] and n-C<sub>10</sub> [128,134–138] hydroconversion data using this criterion shows intrinsic differences in alkane hydroconversion between MFI- and MEL-type zeolites. Simulated C<sub>10</sub> adsorption data are then used to explain the observed differences in the hydroconversion of n-C<sub>10</sub> and of complex feedstocks, and the absence of such differences in a publication [131] on the hydroconversion of n-C<sub>7</sub>.

## 4.2.1 Results and Discussion

 $C_7$  hydroconversion mechanism: The hydroconversion of n- $C_7$  on MFI- [133] and



**Figure 4.8:** Sketch of the MFI- and MEL-type channel intersections. The zeolites have a similar pore diameter (0.55 nm) and structure. The principle difference is that MFI contains both straight and sinusoidal channels, while all MEL-type channels are straight. There is only one MFI-type channel intersection. MEL-type channel intersections are either large (top) or small (bottom).

MEL-type [131] zeolites can be described as a series of consecutive reactions [139]. First, n-C<sub>7</sub> hydroisomerizes into iso-heptane (i-C<sub>7</sub>), then into di-branched heptanes (henceforth referred to as ii-C<sub>7</sub>), which subsequently hydrocrack into iso-butane (i-C<sub>4</sub>) and propane (C<sub>3</sub>) [87, 139] (see eqn. 4.1)

The equilibration between the different  $C_7$  isomers occurs inside the MFI- and MEL-type pores. It is not necessarily observed directly in the product distribution due to the interference of diffusion and -occasionally- of premature hydrocracking.

Diffusion affects the product slate by selectively trapping the slowly diffusing i- $C_7$  [108, 140, 141] and the even more slowly diffusing ii- $C_7$  with proximate methyl groups [89, 142–145] inside the MFI- and MEL-type pores. The more slowly a  $C_7$  isomer diffuses, the greater the chance that it is hydroisomerized into ii- $C_7$  with either *geminal* methyl groups or with methyl groups separated by one methylene (- $CH_2$ -) group (quasi-*vicinal* methyl groups). These are subsequently hydrocracked into a fast-diffusing i- $C_4/C_3$  product pair.

Premature hydrocracking affects the product slate when a  $C_7$  isomer is hydrocracked before it has hydroisomerized into *geminal* or quasi-*vicinal* ii- $C_7$ . It yields an n- $C_4/C_3$  instead of an i- $C_4/C_3$  product pair [21, 87, 111, 146]. It occurs when there are multiple transformations at acid sites inside pores that significantly limit sorbate mobility [87, 146–148]. This happens when the hydrogenation function is insufficiently active as compared to the acid function [10, 11, 112, 146], or when the mass transport between the hydrogenating sites and the acid sites is the rate limiting step [10, 112, 133, 146].

 $C_{10}$  hydroconversion mechanism: It has been shown that n-C<sub>7</sub> and n-C<sub>10</sub> share essentially the same hydroconversion mechanism [15, 21, 111, 149, 150]. The only

difference between n-C<sub>7</sub> and n-C<sub>10</sub> is that the latter can hydroisomerize into a tribranched "iii-C<sub>10</sub>" isomer with both *geminal* and quasi-*vicinal* methyl groups (i.e. with methyl groups on  $\alpha$ ,  $\alpha$ ,  $\gamma$  positions) [15, 17, 18, 21, 149–151] before hydrocracking, whereas the former is too short to form the equivalent iii-C<sub>7</sub> hydrocracking precursor. This difference is irrelevant when studying MFI- (and MEL- [128]) type frameworks, because the shape selective constraints imposed by these frameworks impede the formation of the transition state required for such iii-C<sub>10</sub> isomers [89, 128, 152]. Thus, for the purpose of this chapter, the hydrocconversion of n-C<sub>10</sub> may be regarded as completely analogous to that of n-C<sub>7</sub>: n-C<sub>10</sub> hydroisomerizes into iso-decane (i-C<sub>10</sub>), di-branched decanes (henceforth referred to as ii-C<sub>10</sub>), and subsequently ii-C<sub>10</sub> hydrocracks to give four product pairs - a mono-methyl alkane i-Cx and a linear alkane n-C<sub>(10-x)</sub> (x an integer,  $4 \le x \le 7$ ) [16]:

$$n - C_{10} \rightleftharpoons i - C_{10} \rightleftharpoons ii - C_{10} \to i - C_x + n - C_{10-x}$$

$$(4.2)$$

As with n-C<sub>7</sub> hydroconversion, the more the n-C<sub>10</sub> hydroconversion rate is determined by the rate of the acid-catalyzed reactions, rather than by the mass transport or the hydrogenation rate, the higher the proportion of branched alkanes in the product slate [103].

In view of the striking similarity of the n- $C_7$  and the n- $C_{10}$  hydroconversion mechanism it is intriguing why MEL-type zeolites reportedly have a higher n- $C_{10}$  hydroisomerization selectivity than MFI-type zeolites [128], but not a higher n- $C_7$  hydroisomerization selectivity [131]. This study attempts to resolve this puzzle. To some degree resolution can be obtained by scrutinizing the published n- $C_{10}$  hydroconversion data.

Criteria for identifying mass transport or hydrogenation rate limitations: The intrinsic shape selective properties of zeolites can only be compared when the acidcatalyzed reactions inside the zeolite pores determines the overall alkane hydroconversion rate [103], i.e. in the absence of premature hydrocracking due to mass transfer or hydrogenation rate limitations. In principle, it should be straightforward to identify MFI- and MEL-type zeolite catalysts in which the acid catalysis step determines the alkane hydroconversion rate, for these catalysts characteristically i) yield a primary (i.e. before secondary reactions) hydrocracking product slate consisting of equal amounts of linear and branched alkanes (equation 4.2, ii) yield a primary C7 fraction consisting exclusively of i- $C_7$  (equation 4.2), iii) yield a primary  $C_5$  fraction consisting of equal amounts of n- $C_5$  and i- $C_5$  (equation 4.2), and iv) have a low (primary and secondary) hydrocracking selectivity [10, 11, 103, 112]. In practice, consecutive hydrocracking and hydroisomerization yield a secondary product slate interfering with a straightforward identification [134]. The primary i- $C_7$  isomers are particularly prone to consecutive reactions, because they are the most reactive [12,21,111], and because they will stay adsorbed longer than the other primary hydrocracking products will [153]. By contrast, the  $C_5$  isomers are relatively unreactive [12, 21, 111] and are short enough to desorb rapidly (and stay desorbed) due to competitive adsorption with longer molecules [153]. Thus, a  $C_5$  fraction consisting of equal amounts of  $n-C_5$ and i- $C_5$  (iii) and a low hydrocracking selectivity (iv) are the least affected by secondary reactions, and -therefore- are the most straightforward criteria for identifying

MFI- and MEL-type zeolite catalysts in which the acid catalysis step determines the alkane hydroconversion rate.

Mass transport or hydrogenation rate limitations: An examination of the published n-C<sub>10</sub> hydroconversion data (Table 4.4 [128, 134–137]) shows that only one paper [134] discusses an MFI-type zeolite catalyst that yields a secondary hydrocracking product slate with a C<sub>5</sub> fraction consisting of close to 50% i-C<sub>5</sub>. At 46% n-C<sub>10</sub> hydroconversion, this catalyst looses only 7% of the  $C_{10}$  feed through hydrocracking (%  $C_{10}$ hydrocracked, Table 4.4), whereas at that same conversion level the other catalysts loose more than 35% of the  $C_{10}$  feed [128, 135–137]. This low primary hydrocracking selectivity, the small amount of secondary hydrocracking (mol  $C_7$  hydrocracked/100 mol  $C_{10}$  hydrocracked) at a high % n- $C_{10}$  hydroconversion, and the high percentage of branched alkanes in the secondary hydrocracking product slate (1/5) (Table 4.4, also explains formula), all indicate that this particular MFI-type zeolite catalyst exhibits minimal mass transport and hydrogenation rate limitations [10, 11, 103, 112]. The other tabulated MFI-type zeolite catalysts yield significantly less than 50% i- $C_5$ and have a high hydrocracking selectivity (Table 4.4) characteristic for hydroconversion dominated by the mass transport or hydrogenation rate and not by the acidcatalyzed steps. They employ crystals that are too large, have too high an acid site density or are operated at such a low hydrogen partial pressure [10, 16] that the  $C_{10}$ mass transport rate between the acid sites inside the crystals and the (de-) hydrogenation sites at the crystal's surface [103] is rate limiting [112,146]. Remarkably, also very small MFI-type zeolite crystals cluttered with amorphous debris from a prematurely aborted zeolite synthesis exhibit the high hydrocracking selectivity (4-5%  $C_{10}$  hydrocracked at 8-9% conversion [138], cf. Table 4.4) that is characteristic for mass transport or hydrogenation rate limitations. The preponderance of studies on Pt-loaded MFItype zeolite catalysts in which the n- $C_{10}$  hydroconversion rate was not dominated by the acid catalyzed reactions could explain why the premature i-C<sub>10</sub> hydrocracking used to be considered so important [103, 128, 134, 137].

In addition to an MFI-type zeolite catalyst, there is a MEL-type zeolite catalyst for which  $n-C_{10}$  hydroconversion data have been published, and that meets the % i-C5 criterion and that shows a low hydrocracking selectivity (Table 4.4), indicating that intra-crystalline acid catalyzed reactions determine the n-C<sub>10</sub> hydroconversion rate [128]. This MEL-type zeolite catalyst does not suffer from mass transport limitations, even under conditions where an equivalent MFI-type zeolite does [128] (Table 4.4). When comparing the two catalysts without mass transport limitations [128,134], the MEL-type zeolite hydroisomerizes a higher percentage of the feed than the MFItype zeolite catalyst (Table 4.4). Both the higher threshold for mass transport limitations and the higher hydroisomerization selectivity of the MEL-type zeolite indicate that branched  $C_{10}$  isomers have a lower chance for being converted when they are inside MEL-type pores than when they are inside MFI-type pores. This implies that the MEL-type zeolite either has an intrinsically lower consecutive-reaction rate or an intrinsically higher  $C_{10}$  diffusion rate than the MFI-type zeolite. So far there is no indication of a major difference in  $n-C_{10}$  or  $i-C_{10}$  diffusion rate between MEL- and MFItype zeolites [108] suggesting that the difference must lie in the consecutive-reaction rate [128].

**Table 4.4:** The crystal size, the framework aluminiumdensity (N(Al) in atoms per unit cell), and zeolite type of catalysts operated at a partial hydrogen (p H<sub>2</sub> (kPa)), hydrocarbon pressure (p n-C<sub>10</sub> (kPa)), molar hydrogen-to-hydrocarbon ratio (H<sub>2</sub>/n-C<sub>10</sub> (mol/mol)) require a certain temperature for 50% n-C<sub>10</sub> hydroconversion (T<sub>50%</sub> (K)).

Zeolite type	MFI	MFI	MFI	MFI		MFI		MEL
Crystal size (µm)	n.p. <sup>a</sup>	15	6	4x6		0.1x0.5		4x6
N(Al) (at/u.c.)	5.2	2.5	1.6	3		1.6		3
$p H_2$ (kPa)	100	101	350	100		2000		100
$p n-C_{10}$ (kPa)	1.4	0.7	0.9	1.5		20		1.5
$H_2/n-C_{10} \text{ (mol/mol)}$	71	151	389	65		100		65
$T_{50\%}$ (K) <sup>b</sup>	440	440	440	400		520		430
% n-C <sub>10</sub> hydroconversion	4	$7^b$	$12^{b}$	$10^b$	46		$93^b$	$49^b$
% C <sub>10</sub> hydrocracked	$3-4^{b}$	5	7	5	7		50	5
% i-C <sub>5</sub>	$25^{b}$	31	$42^b$	44	n.p. <sup>a</sup>		$49^b$	$50^{b}$
$1/5\sum_{x=4}^{7}\%$ i-C <sub>x</sub>	$19^{b}$	23	$34^b$	35	n.p. <sup>a</sup>		$47^b$	$41^b$
$mol C_7$ hydrocracked/	0	1	$3^b$	2	$\hat{4}^b$		n.p. <sup>a</sup>	$1^b$
100 mol $C_{10}$ hydrocracked							1	
Reference	[135]	[136]	[137]	[128]	[134]		[134]	[128]

*Note.* At a % n-C<sub>10</sub> hydroconversion the catalyst hydrocrack a certain percentage of the feed (% C<sub>10</sub> hydrocracked), and they yield a percentage branched isomers in the secondary hydrocracking product slate  $(1/5 \sum_{x=4}^{7}\% \text{ i-C}_x, \text{ with }\% \text{ i-C}_x$  the percentage of i-C<sub>x</sub> in each of the the four C<sub>x</sub> fractions, and divided by five to account for the intrinsically linear C<sub>3</sub> fraction) and in the C<sub>5</sub> fraction (% i-C<sub>5</sub>). As only heptane (C<sub>7</sub>) isomers are liable to secondary hydrocracking [12, 21, 136] the extent of secondary hydrocracking is referred to as "mol C<sub>7</sub> hydrocracked / 100 mol C<sub>10</sub> hydrocracked". It was calculated by halving the difference between the molar C<sub>3</sub> and C<sub>7</sub> yield per 100 mol of hydrocracked decane (C<sub>10</sub>). The n-C<sub>10</sub> hydroconversion catalysts that we discuss were loaded with either 0.5 [134, 135] or 1.0 wt-% Pt [128, 136–138]. For comparison, the n-C<sub>7</sub> hydroconversion catalysts were loaded with 0.4 wt-% Pt [131]. <sup>a</sup> np, not published.

<sup>b</sup> Estimated graphically.

**Table 4.5:** The branched primary hydrocracking products ([i- $C_x$ ] (mol/100 mol n,m-diMe- $C_8$  hydrocracked)) from the MFI- and MEL-type zeolites [96, 134] and their dimethyl octane precursors ([n,m-diMe- $C_8$ ] (mol-%) with methyl positions n and m) assuming no preferential hydrocracking into small or large i- $C_x$ .

Products	MFI	MEL	Precursors	MFI	MEL
$[i-C_4]$	15-11 <sup>a</sup>	26	[22-diMe-C <sub>8</sub> ]	$0-5^{b}$	$0-2^{b}$
[i-C <sub>5</sub> ]	19	19	[33-diMe-C <sub>8</sub> ]	14-19	17-19
[i-C <sub>6</sub> ]	$28-32^{a}$	16	[44-diMe-C <sub>8</sub> ]	46-64	28-31
[i-C <sub>7</sub> ]	38	40	[24-diMe-C <sub>8</sub> ]	30-12	52-48
			[35-diMe-C <sub>8</sub> ]	10-0	4-0

<sup>*a*</sup>The mass balance dictates that  $[i-C_7] + [i-C_6] + [i-C_5] + [i-C_4] = 100 \text{ mol}/100 \text{ mol}$  hydrocracked.

 $^{b}$ [n,m-diMe-C<sub>8</sub>] is in mol

Primary hydrocracking product slates: Reconstruction of the primary hydrocracking product slates from the secondary hydrocracking product slates sheds some light on the different reactions that follow the formation of i-C<sub>10</sub>. As discussed above, the composition of the  $C_5$  fraction will be the same in both the primary and the secondary hydrocracking product slate, but all other product fractions require reconstruction. The effects of secondary ii- $C_7$  hydrocracking can be eliminated by adding one ii-C7 molecule to the C7 fraction for each set of one i-C4 molecule and C3 molecule removed from their respective product fractions until there are equal amounts of C<sub>3</sub> and C7. This yields the primary C3 fraction. The resultant C4 fraction is representative for the primary  $C_4$  fraction as well, for secondary hydroisomerization of  $C_4$ is unlikely. The effects of secondary hydroisomerization on the resultant  $C_7$  fraction can be eliminated, because the hydrocracking mechanism stipulates that the primary  $C_7$  fraction consists for 100% out of i- $C_7$ . Applying this procedure to the secondary hydrocracking product slate of the MEL-type zeolite (Figure 4.9B) yields virtually complete primary i- $C_4$ /n- $C_6$  and i- $C_6$ /n- $C_4$  product pairs (Figure 4.9D), indicating that the C<sub>6</sub> fraction has remained relatively unaffected by secondary reactions. Construction of a secondary hydrocracking product slate of the MFI-type zeolite based on the published data [134] (Figure 4.9A), requires making the assumption that the composition of the carbon number fractions does not drastically change when the conversion is increased from 46% to 93% n- $C_{10}$  conversion. If we apply our procedure to turn this secondary hydrocracking product slate into a primary one (Figure 4.9C), the C<sub>6</sub> fraction contains 10% too much i-C<sub>6</sub> to complete the primary i-C<sub>4</sub>/n-C<sub>6</sub> and  $i-C_6/n-C_4$  product pairs. Therefore  $i-C_6$  and  $i-C_4$  data are within the tabulated 15% error margin (Table 4.5).

**Experimental ii**- $C_{10}$  **selectivity:** On the basis of the hydrocracking mechanism [21, 149, 150](Figure 4.10), it is possible to link the individual components of the primary  $C_{10}$  hydrocracking product slate (Table 4.5, Figure 4.9 C,D) to their ii- $C_{10}$  precursors through four linear equations. Each 100 mol of ii- $C_{10}$  consists of [n,m-diMe-



**Figure 4.9:** The secondary (top, A and B) and primary (bottom, C and D) hydrocracking product slates of the MFI- (left, A and C) and the MEL-type zeolite (right, B and D) at 46% and 49%  $n-C_{10}$  hydroconversion respectively [128, 134]: normal (white) and branched (black) isomer yield.

 $C_8$ ] mol of n,m-dimethyl octane, and hydrocracks into a known number of moles of branched isomers, [i- $C_x$ ]. With these definitions in place, the individual hydrocracking reactions (Figure 4.10) can be described as:

$[2, 2 - diMe - C_8]$	+	$u \cdot [2, 4 - diMe - C_8]$	=	$[i - C_4]$	(4.3)
$[3, 3 - diMe - C_8]$	+	$v \cdot [3, 5 - diMe - C_8]$	=	$[i-C_5]$	(4.4)
$w \cdot [4, 4 - diMe - C_8]$	+	$(1-v)\cdot[3,5-diMe-C_8]$	=	$[i - C_6]$	(4.5)
$(1-w) \cdot [4, 4 - diMe - C_8]$	+	$(1-u)\cdot[2,4-diMe-C_8]$	=	$[i - C_7]$	(4.6)

In these equations u, v and w are the probabilities that 2,4-, 3,5- and 4,4-diMe-C<sub>8</sub> split off either a small (u, v, w > 0.5) or a long (u, v, w < 0.5) iso-alkane. Assuming that the ii-C<sub>10</sub> precursors have no strong preference for splitting either way (u  $\approx$  v  $\approx$  w  $\approx$  0.5) the solutions for the above 4 equations severely limit the possible ii-C<sub>10</sub> hydrocracking precursors (Table 4.5).

In summary, a scrutiny of the published  $n-C_{10}$  hydroconversion data shows that of the two kinetically favored ii- $C_{10}$  molecules (Figure 4.11), the MFI-type zeolite predominantly hydrocracks the *geminal* ii- $C_{10}$  (4,4-diMe- $C_8$ ), whereas the MEL-type zeolite predominantly hydrocracks the quasi-*vicinal* ii- $C_{10}$  (2,4-diMe $C_8$ ) (Table 4.5). We can now turn to the free energies of formation as amenable by molecular simulations to see why there is such a marked difference in intrinsic shape selectivity.

**Simulated ii-C**<sub>10</sub> **selectivity:** The free energy of formation of the individual ii-C<sub>10</sub> hydrocracking precursors inside the MFI- and MEL-type zeolites shed some light on



**Figure 4.10:** Overview of the n-C<sub>10</sub> hydroconversion [21, 134]: equilibration between isomers with (•—•) or without (•…•) a change in the degree of branching and hydrocracking (—). Of all the ii-C<sub>10</sub> isomers only those with *geminal* or quasi-*vicinal* methyl groups are shown. The ii-C<sub>10</sub> isomers with no *geminal* or quasi-*vicinal* methyl groups hydrocrack  $\sim 10^2$  times more slowly than the isomers shown [15, 17, 151]. This leaves them ample time to hydroisomerize into ii-C<sub>10</sub> isomers with *geminal* or quasi-*vicinal* methyl groups. They do so at a rate that is  $\sim 10^3$  times faster than their hydrocracking rate [15]. Thus, the hydrocracking will be dominated by the ii-C<sub>10</sub> isomers that are shown. The individual hydroisomerization and hydrocracking steps are elucidated in Figures 4.11 and 4.12.

the postulated differences in hydrocracking precursors. As indicated by a lower free energy of formation, MFI-type zeolites preferentially form *geminal* ii-C<sub>10</sub>, whereas MEL-type zeolites preferentially form quasi-*vicinal* ii-C<sub>10</sub> (Table 4.6). The reason for this selective decrease in free energy (Table 4.6) is that the shape of the MFI-type intersection (Figure 4.8A) is commensurate with that of *geminal* ii-C<sub>10</sub>, whereas the shape of the larger MEL-type intersection (Figure 4.8B) is commensurate with that of quasi-*vicinal* ii-C<sub>10</sub> (Figure 4.13). Thus, the intersections constitute a mould for the formation of particular hydrocracking precursors. Once formed, the hydrocracking precursors will be trapped at the intersections, for they diffuse too slowly [89, 140] to leave the pores intact. The preference of MFI-type zeolites for *geminal* instead of quasi-*vicinal* ii-C<sub>10</sub> becomes more evident when the temperature is increased from 415 K to 523 K. Thus, the decreased free energy of formation of *geminal* ii-C<sub>10</sub> inside MFI-type zeolites and of quasi-*vicinal* ii-C<sub>10</sub> inside MEL-type zeolites supports the empirical observation that there is an intrinsic difference in their hydrocracking functionality, and offers an explanation of why that is so.

**Simulated ii-C**<sub>7</sub> **selectivity:** The adsorption properties of ii-C<sub>7</sub> hydrocracking precursors (Table 4.7) are analogous to those of ii-C<sub>10</sub> (Table 4.6). Again MFI-type zeolites lower the free energy of formation of ii-C<sub>7</sub> with *geminal* methyl groups and MEL-type zeolites lower that of the ii-C<sub>7</sub> with quasi-*vicinal* methyl groups (viz. 2,4-dimethyl pentane). Since n-C<sub>10</sub> and n-C<sub>7</sub> hydroconversion are analogous, we would expect that MFI-type zeolites preferentially hydrocrack *geminal* ii-C<sub>7</sub>, whereas MEL-


**Figure 4.11:** The (protonated) cyclopropyl transition state ( $\bigtriangledown$  and  $\triangle$ ) and the products for the hydroisomerization of i-C<sub>10</sub> into ii-C<sub>10</sub>. A) 2-Me-C<sub>9</sub> hydroisomerization into **2,2-**, 2,3-, **2,4-**, 2,5-, 2,6-, 2,7-diMe-C<sub>8</sub>; B) 3-Me-C<sub>9</sub> into **3,3-**, 3,4-, **3,5-**, 3,6-, 2,6-diMe-C<sub>8</sub>; C) 4-Me-C<sub>9</sub> into **3,3-**, 2,3-, **4,4-**, 4,5-, **3,5-**, 2,5-diMe-C<sub>8</sub>; D) 5-Me-C<sub>9</sub> into 3,4-, **2,4-**, **4,4**-diMe-C<sub>8</sub> [21]. Hydrocracking precursors are shown in bold. The probabilities of formation of the isomers are given, assuming no preferential formation for any i-C<sub>10</sub> isomer or transition state. The shape selectivity imposed by the MEL- and MFI-type zeolites shifts the probability towards the ii-C<sub>10</sub> and i-C<sub>10</sub> isomers that have a shape commensurate with the MEL- and MFI-type pores [89]. Of the alkanes with *geminal* methyl groups 4,4-diMe-C<sub>8</sub> is favored. The probability for 4,4- and 2,4-diMe-C<sub>8</sub> formation is further increased, because 5-Me-C<sub>9</sub> appears to be the i-C<sub>10</sub> isomer preferentially retained [108, 141] and formed (Figure 4.14, Table 4.8) by both MEL- and MFI-type zeolites.



**Figure 4.12:** Transitions states and intermediates for the hydrocracking of ii-C<sub>10</sub> isomers with *geminal* or quasi-*vicinal* methyl groups [134]. As all carbo-cationic and alkene intermediates leave the catalysts as alkanes, carbo-cations and alkenes with the same carbon backbone will end up as identical products, and are grouped together as such.

**Table 4.6:** Gas phase free energy of formation  $(\Delta G_{gas}^f \text{ (kJ/mol)})$  (from literature [22] data), free energy of adsorption  $(\Delta G_{ads} \text{ (kJ/mol)})$ , heat of adsorption  $(\Delta H_{ads} \text{ (kJ/mol)})$ , and free energy of formation inside a zeolite  $(\Delta G_{zeo}^f \text{ (kJ/mol)})$  for decane isomers in MFI- or MEL-type silicas at 415 K.

		MFI	MEL	MFI	MEL	MFI	MEL
$C_{10}$ isomer	$\Delta G_{qas}^{f}$	$\Delta G_{ads}$	$\Delta G_{ads}$	$\Delta H_{ads}$	$\Delta H_{ads}$	$\Delta G^f_{zeo}$	$\Delta G^f_{zeo}$
	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
$n-C_{10}$	150	-54	-49	-113	-112	96	101
$2-Me-C_9$	147	-53	-47	-112	-108	94	99
$5-Me-C_9$	150	-53	-52	-115	-113	96	98
22-diMe-C8	145	-48	-38	-105	-100	98	107
33-diMe-C <sub>8</sub>	147	-46	-37	-102	-97	101	110
44-diMe-C <sub>8</sub>	147	-50	-39	-106	-99	97	108
24-diMe-C <sub>8</sub>	150	-42	-55	-114	-117	108	96
35-diMe-C <sub>8</sub>	147	-37	-52	-106	-114	111	96
335-trMe-C	7 154	-20	-22	-76	-91	134	132



**Figure 4.13:** Schematic drawing of the thermodynamically preferred positions of Left) 4,4diMe-C<sub>8</sub> inside MFI-type zeolite, with octyl group in the straight channel and the methyl groups protruding into the sinusoidal channel, Right) 2,4-diMe-C<sub>8</sub> inside MEL-type zeolite, with a hexyl group in one straight channel and an iso-butyl group protruding into another straight channel. Alkanes are shown as ball-and-stick models, frameworks as sticks only. Top and bottom views are at a 90 angle from each other.

**Table 4.7:** Gas phase free energy of formation  $(\Delta G_{gas}^{f} \text{ (kJ/mol)})$  [22], change of free energy of formation by zeolite ( $\Delta G_{ads} \text{ (kJ/mol)}$ ), heat of adsorption ( $\Delta H_{ads} \text{ (kJ/mol)}$ ), and free energy of formation inside a zeolite ( $\Delta G_{zeo}^{f} \text{ (kJ/mol)}$ ) for heptane isomers in MFI- or MEL-type silicas at 523 K.

		MFI	MEL	MFI	MEL	MFI	MEL
C <sub>7</sub> isomer	$\Delta G_{gas}^{f}$	$\Delta G_{ads}$	$\Delta G_{ads}$	$\Delta H_{ads}$	$\Delta H_{ads}$	$\Delta G_{zeo}^f$	$\Delta G_{zeo}^f$
	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
n-C <sub>7</sub>	167	-27	-24	-78	-76	140	143
$2-Me-C_6$	164	-27	-25	-80	-79	137	140
$3-Me-C_6$	164	-26	-24	-78	-77	138	140
22-diMe-C	5 167	-24	-14	-74	-67	143	153
33-diMe-Ca	5 168	-18	-8	-68	-62	150	160
24-diMe-Ca	5 169	-13	-27	-73	-82	156	142
23-diMe-C	5 163	-25	-20	-78	-76	138	143

type zeolites prefer the quasi-*vicinal* ii- $C_7$ . Unfortunately this difference in the hydrocracking pathway is difficult to quantify, as the individual ii- $C_7$  precursors do not leave their signature in the  $C_7$  hydrocracking product slate (equation 4.2).

**ii-C**<sub>10</sub> **versus ii-C**<sub>7</sub> **hydrocracking:** The difference in hydrocracking pathway between the MFI- and MEL-type zeolite can explain why an MFI-type zeolite hydrocracks a higher percentage of C<sub>10</sub> feed but not of C<sub>7</sub> feed. Kinetic data show that at low temperatures (below 460-500 K) the *geminal* di-methyl alkanes preferred by the MFI-type zeolite have the highest hydrocracking rate, whereas at higher temperature (above 460-500 K) the quasi-*vicinal* di-methyl alkanes preferred by the MEL-type zeolite have the highest hydrocracking rate [17, 18, 151]. Since zeolites that hydrocrack alkanes at a higher rate will also hydrocrack a larger percentage of the feed, this can explain why MFI-type zeolites (at 400, 440, or 520 K) hydrocrack more C<sub>10</sub> than MEL-type zeolites (at 430 K) (Table 4.4), but not more C<sub>7</sub> (all comparative tests at 523 K [131]). Although the low C<sub>10</sub> and high C<sub>7</sub> hydroconversion test temperature can explain the low C<sub>10</sub> and high C<sub>7</sub> hydrocracking selectivity of the MEL-type zeolite, it fails to explain why MEL-type zeolites reportedly have lower hydrocracking selectivity than MFI-type zeolites at temperatures as high as 655 K [129].

**Simulated competitive adsorption:** An alternative explanation for the differences in alkane hydrocracking between MFI- and MEL-type zeolites follows from the dramatic selectivity difference that shows up in a study on the adsorption from mixtures of equal amounts of gaseous n-C<sub>10</sub> and i-C<sub>10</sub>. Both at low loading (Table 4.6) and at high loading (Figure 4.14A), MFI-type zeolites adsorb n-C<sub>10</sub> or i-C<sub>10</sub> in approximately equal amounts, indicating that molecule-molecule interactions have only a minor effect on the free energy of adsorption (~1 kJ/mol change) in MFI-type zeolites. In marked contrast, MEL-type zeolites develop a strong preference for linear



**Figure 4.14:** The adsorption isotherm at 415 K as calculated by CBMC calculations of a binary mixture of a) 50% 2-methyl nonane and 50% n-decane b) 50% 5-methyl nonane and 50% n-decane. MFI-type (left) and MEL-type silica (right).

alkanes at high loading (Figure 4.14B). This preference corresponds to a decrease in the free energy of the adsorption (and of formation) of  $n-C_{10}$  relative to that of  $i-C_{10}$ of 4-5 kJ/mol (Table 4.8). A probable cause for the decrease in free energy of the linear alkanes relative to that of the branched alkanes is that the former can fill the pores with a higher packing efficiency (retaining a higher entropy) than the latter [33, 61]. Closer inspection of the molecules shows that approximately half of the 4 MFI-type intersections per unit cell contain  $i-C_{10}$  molecules, whereas slightly fewer than half of the 2 large MEL-type intersections per unit cell still contain  $i-C_{10}$  at full loading. CBMC calculations indicate that full loading is obtained at 20 kPa  $C_{10}$ , at temperatures up to 570 K and above 1 kPa  $C_{10}$ , at temperatures near 415 K, i.e. at the  $n-C_{10}$ hydroconversion conditions discussed here (Table 4.4).

**Competitive adsorption in n-C**<sub>10</sub> **hydroconversion:** At full loading, moleculemolecule interactions impede formation of i-C<sub>10</sub> out of n-C<sub>10</sub> by increasing the free energy of formation of the former at the large MEL-type intersections. In addition, they impede hydroisomerization reactions following the formation of i-C<sub>10</sub> by facilitating the (re-)adsorbtion of n-C<sub>10</sub> at the cost of the (re-)adsorption of i-C<sub>10</sub>. In MFI-type zeolites molecule-molecule interactions have no such marked effect (Tables 4.6 and 4.8). The formation of ii-C<sub>10</sub> hydrocracking precursors from i-C<sub>10</sub> by consecutive hydroisomerization reactions is further impeded by the limited availability of suitable sites in the MEL-type zeolites at full loading. There are only half as many large MEL-type intersections as there are MFI-type intersections (Figure 4.8). Both the higher selectivity for absorbing linear instead of branched alkanes and the lower density of sites suitable for forming hydrocracking precursors will suppress consecutive hydrocracking reactions, and explain the lower hydrocracking selectivity (and

i-C <sub>10</sub>	MFI empty	MFI full	MEL empty	MEL full
isomer	$\Delta G_i^{ads} - \Delta G_n^{ads}$			
	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
$2-Me-C_9$	0.8	1.8	1.7	5.7
$5-Me-C_9$	0.4	-0.9	-2.5	2.9

**Table 4.8:** Effect of molecule-molecule interactions on the difference in the free energy of adsorption between i- $C_{10}$  and n- $C_{10}$  ( $\Delta G_i^{ads} - \Delta G_n^{ads}$  (kJ/mol)).

*Note* We compare an "empty" zeolite (Henry regime, no molecule-molecule interactions, Table 4.6) with a "full" zeolite that is in equilibrium with a mixture consisting of equal amounts  $n-C_{10}$  and  $i-C_{10}$  at high loading (Figure 4.14).



**Figure 4.15:** The adsorption isotherm at 523 K as calculated by CBMC calculations of a binary mixture of a) 50% 2-methyl hexane and 50% n-heptane. MFI-type (left) and MEL-type silica (right).

higher hydroisomerization selectivity) of MEL-type zeolites.

No competitive adsorption in n-C<sub>7</sub> hydroconversion: Interestingly, the adsorption simulations not only explain why the MEL-type zeolite has a higher n-C<sub>10</sub> hydroisomerization selectivity than the MFI-type zeolite, they also explain why this is not the case for the n-C<sub>7</sub> hydroisomerization [131] selectivity. The comparative n-C<sub>7</sub> hydroconversion tests where done at 10 kPa n-C<sub>7</sub>, 523 K [131]. At this temperature and pressure MFI- and MEL-type zeolites have a low enough loading (about one molecule per unit cell) for n-C<sub>7</sub> and i-C<sub>7</sub> to have a comparable free energy of formation in both MFI- and MEL-type zeolites (Figure 4.15). In addition, there is no shortage of available sites at the intersections of these zeolites to form hydrocracking precursors. Thus, the n-C<sub>7</sub> hydroconversion tests were done at too low a C<sub>7</sub> loading for competitive adsorption of n-C<sub>7</sub> and i-C<sub>7</sub> to occur and so demonstrate the intrinsic selectivity differences between MFI- and MEL-type zeolites.

Actual hydrodewaxing tests: It is difficult to judge what the adsorption properties of MEL- and MFI-type zeolites are when a complex feedstock with alkanes significantly longer than  $C_{10}$  is converted at a temperature as high as 655 K (instead of the 430-523 K used for  $C_7$  and  $C_{10}$ ) [129]. We are tempted to conclude that competitive adsorption between linear alkanes and branched alkanes will occur. In that case the lower density and lower accessibility of the large MEL-type intersections as compared to the MFI-type intersections will overrule the enhancement of the hydrocracking selectivity of MEL-type zeolite by the high operation temperature. To found such a conclusion more firmly would require more experimental studies quantifying the separate effects of temperature and loading on the alkane hydroconversion selectivity of MEL- and MFI-type zeolites.

#### 4.3 Heptadecane conversion on TON-type zeolites

This section briefly returns to the subject of long-chain alkane conversion on mediumpore zeolites (in this case TON). The difference between section 1 and this section is the addition of diffusional aspects into the analysis. As already mentioned, in dewaxing the aim is to convert long-chain hydrocarbons (waxes) into branched isomers. Hydrocracking is an undesirable side reaction that should be suppressed as much as possible. Figure 1.4 shows that the di-methyl alkanes that most easily hydrocrack (alkanes with proximate methyl groups), have a relatively high Gibbs free energy of formation in TON-type zeolites. Figure 4.16 shows that TON-type zeolites instead favor the formation of di-branched alkanes with the methyl group separated by two or more methylene groups. 2,6- and 2,10-dimethylpentadecane (dmpd) have the lowest Gibbs free energy of formation. The shape of these two isomers is commensurate with periodicity of the cavities in the TON-type zeolite channel (see Figure 4.17). For the other isomers there is no such perfect match between the spacing of the methyl groups and that of the undulations in the TON-type channels. Figure 4.16 shows that commensurate 2,6- and 2,10-dmpd have a barrier of 15  $k_BT$ , giving a diffusion coefficient of  $2x10^{-13}$  m<sup>2</sup>s<sup>-1</sup> and that the diffusion of the incommensurate 2.7- or 2.9-dmpd is virtually unhampered. From this Figure we can deduce the Gibbs free energy of



**Figure 4.16:** Gibbs free energy as a function of the position of the 2,m-dimethylpentadecane isomers in TON-type zeolites.

formation of the various 2,m isomers. The incommensurate isomers have a similar Gibbs free energy while the commensurate 2,6 dmpd has a 5  $k_B$ T lower Gibbs free energy of formation. In the gas phase or in a wide pore zeolite [17] the barrier for all methyl shifts is only 1.5  $k_B$ T. The Polanyi-Brønsted principle suggests that TON-type zeolites raise this barrier (by some 5  $k_B$ T) for the methyl shift of a commensurate isomer (2,6-dmpd) into an incommensurate one (2,5- or 2,7-dmpd), leaving methyl shifts among incommensurate isomers unaffected. The reason for the relatively high barriers to diffusion of the commensurate intermediates is that the diffusion of a commensurate isomer requires that both methyl groups leave their thermodynamically favourable sites, while the diffusion of an incommensurate molecule always involves one methyl group at an unfavourable position. Therefore a displacement of a commensurate molecule changes the Gibbs free energy more than that of an incommensurate molecule. A similar effect has been observed for clusters of molecules [154].

These simulation results lead to the following alkane hydroconversion mechanism. The commensurate 2,6- and 2,10-dmpd will form preferentially but their barrier for diffusion is higher than their barrier for a methyl shift. Once a methyl shift has taken place, an incommensurate structure has formed which can leave the zeolite. However, 2,5-dmpd can easily methyl shift into 2,4-dmpd, which will hydrocrack before it leaves the zeolite. This suggests that in the product slate we may find some 2,5-, very little 2,6- but a significant amount of 2,7-, 2,8-, and 2,9-dmpd isomers. Aspects of such a product distribution have actually been observed experimentally. Interestingly, these effects were explained in terms of catalysis at the exterior zeolite surface [93] ("pore mouth" and "key lock" catalysis). Our interpretation implies catalysis inside the zeolitic pores. A similar conclusion has been obtained from molecular dynamics simulations [90, 108, 141]. We have also calculated the Gibbs free en-



**Figure 4.17:** Sketch of a commensurate (top) and an incommensurate (bottom) molecule in a TON-type zeolite. If there are three carbon atoms separating the two methyl groups the molecule is commensurate with the zeolite structure. If we displace, for example, a 2,6-dimethylpentadecane (dmpd) isomer both methyl groups have to leave their optimal position. If we displace an incommensurate molecule, for example, the 2,5-dmpd isomer, part of the molecule always remains in an unfavorable configuration. As a consequence, the Gibbs free energy barriers of the incommensurate molecules are much smaller and hence these molecules diffuse faster.

ergy profiles of the 3,m-dmpd isomers. For these isomers we find that 3,7-dmpd is the commensurate molecule. The Gibbs free energy of these 3,m-isomers is  $1-2 k_B T$  higher compared to the 2,m isomers. We therefore expect that the product distribution also contains 3,8-, 3,9-, and 3,10-dmpd isomers in slightly smaller quantities.

#### 4.4 Conclusions

In this chapter we studied the shape selectivity in the hydroconversion of alkanes on medium-pore zeolites. The translation of well-known concepts in zeolite-based shape selective catalysis into thermodynamic properties enables us to explain differences in shape selectivity between zeolites in terms of adsorption thermodynamics.

The good fit between measured and simulated adsorption constants (Henry coefficients and adsorption enthalpies) establishes that normal alkanes with only one methyl group are able to enter the TON-, MTT- and AEL-type pores, and that alkanes with *geminal* methyl groups are not. The shape selective formation of alkanes with (quasi-) *vicinal* methyl groups indicates that these too are able to enter the TON-, MTT- and AEL-type pores, albeit with difficulty. Thanks to this evaluation of the molecular sizes, we are able to rule out that alkanes with one methyl group are predominantly hydroisomerized at the pore mouths. An analysis of the activation energy corroborates this finding. Instead, we can explain the high selectivity of the TON-, MTT-, and AEL-type zeolites for alkanes with terminal methyl groups in terms of product selectivity, and the low selectivity for alkanes with proximate methyl groups in terms of transition state selectivity (Figure 4.1). An unambiguous evaluation of pore mouth catalysis would require studying zeolites that clearly absorb



**Figure 4.18:** The difference in catalytic selectivity between MEL- (left) and MFI-type (right) zeolites in decane hydrocracking. Out of all possible isomers, those are formed that have a shape commensurate with the pore. MEL-type zeolites preferentially form 2,4-dimethyloctane, MFI-type zeolites 4,4-dimethyloctane because these molecules have a shape commensurate with the respective channel intersections. Since hydrocracking of 2,4-dimethyloctane yields iso-butane, while hydrocracking of 4,4-dimethyloctane yields n-butane [21], we now understand why the hydroconversion of n-decane using MEL-type zeolites yields about twice as much iso-butane as that using MFI-type zeolites.

linear alkanes but exclude all branched alkanes.

When the rate of the acid-catalyzed reactions determines the n-C<sub>10</sub> hydroconversion rate, MFI- and MEL-type zeolites hydroisomerize normal alkanes into alkanes with geminal or quasi-vicinal methyl groups before they hydrocrack them. An analysis of the hydrocracking product slates and of the adsorption properties obtained by molecular simulations indicates that MFI-type zeolites intrinsically hydrocrack more geminal and fewer quasi-vicinal di-methyl alkanes than MEL-type zeolites. An illustration of this difference is shown in Figure 4.18. As geminal di-methyl alkanes hydrocrack faster than quasi-vicinal di-methyl alkanes at low temperature, but not at high temperature, the selectivity for geminal di-methyl alkanes explains why MFI-type zeolites hydrocrack more of a  $C_{10}$  feed than a MEL-type zeolite (selectivity tested at low temperature), but not more of a C7 feed (tested at high temperature). The adsorption properties indicate that the higher selectivity of the MFI-type structure for adsorbing branched rather than linear alkane reactants also contributes to its higher hydrocracking selectivity as compared to a MEL-type zeolite. As this higher reactant selectivity is only significant at sufficiently high loading, it also explains why MFI-type zeolites showed higher  $n-C_{10}$  hydrocracking (tested at high loading), but not higher  $n-C_7$  hydrocracking selectivity (tested at low loading) than a MEL-type zeolite.

# VShape selectivity in alkane conversion, studied at elevated pressures<sup>1</sup>

In chapter 4 the effect of zeolite pore topology on shape selective hydroconversions at very low loading is analyzed. Under such conditions the effect of intermolecular interactions can be ignored. Not always are operation conditions such that this assumption holds. As shown in chapter 3, intermolecular interactions become increasingly important at high pressures. The effect of these intermolecular interactions on the selectivity of alkane hydroconversions is studied in the next section.

#### 5.1 Hexadecane conversion on large pore zeolites

In order to fully utilize the structural diversity afforded by the panoply of available molecular sieve structures [2] we need a fundamental understanding of the link between structure and shape selectivity. Traditional theory says that the structures induce shape selective conversion by imposing steric constraints on the reaction (transition state shape selectivity) and on the diffusion rate (product and reactant shape selectivity) [90, 91, 156]. However, this explanation alone is not sufficient to understand shape selectivity [157–162]. A number of additional parameters (such as inverse shape selectivity) have been proposed [3, 93, 156, 160, 161], but these have remained subject to debate [87,89,147,156,163,164]. In a recent attempt to come up with a more systematic approach to shape selectivity we suggested that molecular sieves impose a chemical equilibrium on adsorbed molecules that is different from that in the gas phase [77,88,89,120,165]. In sieves with relatively small pores, and thereforepredominantly molecule-wall interactions, the imposed chemical equilibrium could be successfully ascertained by simulations at low loading [88,89]. However, for sieves with larger pores, the effects of intermolecular interactions at higher loading may need to be considered [77]. One of the aims of this work is to investigate whether adsorbent-adsorbent interactions contribute to the selectivity. In both cases, the Gibbs free energy of adsorption quantifies how a molecular sieve structure and the other adsorbed molecules alter the gas phase Gibbs free energy of formation of a hydrocarbon. By definition, the Gibbs free energy of adsorption is the difference of the Gibbs free energy formation in the gas phase and that in the adsorbed phase. Naturally, ad-

<sup>&</sup>lt;sup>1</sup>This chapter is based on refs. [77, 155]



**Figure 5.1:** Molar ratio of 22DMB/n-C<sub>6</sub> adsorbed (left bar) and of ratio DMB/n-C<sub>6</sub> produced (middle bar) by n-C<sub>16</sub> hydroconversion at 70% C<sub>16</sub> hydrocracking, 577 K,  $3x10^3$  kPa n-C<sub>16</sub>. All catalysts were made equally active by adding nitrogen-containing compound to the feed. Molar ratios were normalized relative to the ratios of FAU-type sieves. The right bar shows the results from the CVFF simulations by Santilli et al. The pore diameter increases from the MTT-type zeolite to the amorphous aluminosilicate (ASA). Data adapted from reference [159].

sorption can only yield a chemical equilibrium different from that in the gas phase as long as the molecular exchange between the adsorbed phase and gas phase is sufficiently slow so as to prevent physical equilibration between the two phases [120, 165]. This tends to be the case at high loading [16,88,120,165,166]. Recent simulations indicate that molecular sieves skew the chemical equilibrium, favoring molecules whose shape is commensurate with that of the pores [88,89]. However, if the pore opening is less than 0.6 nm across, these thermodynamically favored paraffins tend to fit so snugly that they remain trapped. They can be detected only by their consecutive reaction products, which fit less well, and so diffuse out [88, 89, 167, 168]. Interestingly, earlier work by Santilli et al. had suggested that 0.70-0.74 nm diameter pores (as in AFI-type sieves) preferentially adsorb and release the thermodynamically preferred, branched paraffins in n-hexadecane (n-C<sub>16</sub>) hydroconversion [158–160]. This phenomenon was referred to as "inverse shape selectivity" [158-160]. In that instance, the thermodynamic preference for branched paraffins was quantified by physically equilibrating an equimolar gaseous mixture of di-, mono, and non-branched hexane  $(C_6)$  isomers on molecular sieves with various structures [158–160]. The relative preference of various structures for adsorbing branched paraffins appeared to translate into a preference for their formation in hydrocarbon hydroconversion (Figure 5.1) [158-160, 169].

Simulations (using molecular "docking") were then employed to try and understand, at the molecular level, why the selective adsorption of branched rather than linear paraffins would lead to their selective production. These simulations suggested that the variations in adsorption enthalpy related to pore size and could explain the experimental data. The 0.70-0.74 nm pores (as in AFI-type zeolites) would have optimal stabilizing Van der Waals interactions with the branched paraffins, and therefore a minimal adsorption enthalpy [159]. Inside smaller pores (like MTW-type zeolites) the adsorption enthalpy would increase, because the walls would repulse branched paraffins. Inside larger pores (as in FAU-type zeolites), the stabilizing interaction would disappear, because these pores would be so large that adsorbateadsorbent Van der Waals interactions become negligible [159]. Assuming that this variation in adsorption enthalpy with pore size could be extrapolated to the variation of the Gibbs free energy of the transition state for the formation of branched molecules, the "inverse shape selectivity" phenomenon was categorized as an example of transition state selectivity [158, 159]. This represents some of the earliest work to employ molecular simulations to explain, and even predict, the catalytic properties of molecular sieves based on their adsorption properties. The molecular "docking" technique enabled an evaluation of the adsorption enthalpy of paraffins at low loading by using a CVFF force field [159]. It has since become apparent that the CVFF force field is not particularly suited for simulating the forces exerted on branched paraffins [28]. For example, the adsorption isotherms of isobutane by MFI-type silica show a step at approximately half the loading, such a step can not be reproduced with this force field [28]. At the same time, the drastic improvement in computation capabilities has made it possible to simulate entropy and loading effects [33, 170, 171]. Recent configurational-bias Monte Carlo (CBMC) simulations showed how differences in configurational adsorption entropy (packing efficiency) dominated the adsorption in 0.55 nm MFI-type pores from ternary mixtures of  $C_6$  isomers with various degrees of branching, at high loading [33, 170, 171]. The initial motivation of this work was to redo the calculations of Santilli et al. [159] using modern simulation techniques and using contemporary force fields. As we will demonstrate, these improved calculations did not yield an improvement in the prediction of the shape selectivity. In fact, our calculations predict that all large-pore zeolites would give a similar product distribution, which is in disagreement with the experimental data. This suggests that the simulation results of Santilli et al. may have resulted from a cancellation of the errors in the force field and the limitation of the simulation method, which did not allow simulations at conditions approaching the actual reaction conditions. More importantly, our results also suggest that the molecular interpretation of Santilli et al, that inverse shape selectivity can be related to a match of the size of a branched molecule with the diameter of the channel may not be correct. Here, we will demonstrate that the molecular basis of inverse shape selectivity is related to entropic effects inside the zeolite pores under conditions where the zeolites are (almost) fully saturated. This paper focuses on molecular sieves with a pore diameter greater than 0.60 nm. Those with an AFI- type structure receive the most attention, because the majority of the measured data happen to be available for this type of sieve [157–159, 169, 172–176].

Adsorption at low loading In trying to explain the measured adsorption phenomena by molecular simulations, Santilli et al. were hamstrung by the computational limitations of the early 1990s. Because of these limitations, it was expedient to assume that the loading was sufficiently low for intermolecular interactions to be negligible [159], and that differences in adsorption entropy between  $C_6$  isomers were negligible [159]. With these assumptions in place, a good correlation between the

**Table 5.1:** The difference in Gibbs free energy of adsorption between 22DMB and n-C<sub>6</sub> (I) determined from a measured ternary isotherm of an equimolar mixture of 22DMB, 3MP and n-C<sub>6</sub> at 14 kPa C<sub>6</sub>, 403 K,  $\delta\Delta G_{ads22-n}$  (kJ/mol), (II) determined from a simulated binary isotherm with equal amounts of 22DMB and n-C<sub>6</sub> at 14 kPa C<sub>6</sub>, 403 K,  $\delta\Delta G_{14kPa22-n}$  (kJ/mol), and (III) determined at very low loading,  $\delta\Delta G_{CBMC}$  (kJ/mol).  $\delta\Delta H_{CVFF}$  (kJ/mol) and  $\delta\Delta H_{CBMC}$  are the difference in adsorption enthalpy at very low loading determined by molecular "docking" in a CVFF force field and by CBMC, respectively.

Structure	Pore	$\delta \Delta G_{ads22-n}$	$\delta \Delta H_{CVFF}$	$\delta \Delta H_{CBMC}$	$\delta \Delta G_{CBMC}$	$\delta \Delta G_{14kPa22-n}$
type	$size^a$					
code	(nm)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
FAU	1.20	1.3	n.a. <sup>b</sup>	1.6	0.3	2.1
LTL	0.99	3.9	2.7	2.8	0.2	4.1
MAZ	0.75	n.a.	n.a.	0.7	-1.3	-4.4
AFI	0.77	-5.04.5	-5.1	1.1	-0.9	-4.7
MOR	0.64	-0.9	n.a.	5.1	5.4	0.9
BEA	0.64	3.5	n.a.	8.3	10.1	5.8
MTW	0.57	7.2	4.1	19.6	23.4	23.4
VFI	1.27	2.7	0.0	n.a.	n.a.	n.a.

<sup>*a*</sup>Pore diameter from ref. [159] <sup>*b*</sup>Not available.

difference in Gibbs free energy of adsorption determined from the measured ternary isotherms and the difference in adsorption enthalpy obtained in the CVFF force field,  $\delta\Delta H_{CVFF}$  (kJ/mol), was found [159]. This correlation suggests that the explanation for both the preferential adsorption and the preferential production of branched paraffins lies in the variation in adsorption enthalpy with void size [159]. Since the adsorbent-adsorbate Van der Waals interactions have a major effect on the adsorption enthalpy, these were assumed to be the dominant force in both the adsorption and the catalytic production of DMB [159].

The differences in adsorption enthalpy between 22DMB and n-C<sub>6</sub>,  $\delta\Delta H_{CBMC}$  (kJ/mol) simulated by CBMC at low loading, do not match the enthalpy differences obtained in the CVFF force field (Table 5.1). This probably reflects the currently known limitations of the CVFF force field in handling branched paraffins [28]. Consistent with earlier validations [28,33,87,170,171,177], the adsorption enthalpies from the CBMC calculations agree well with the adsorption enthalpies measured using only a single component at low loading (Table 5.2) [41, 109, 173, 174, 178, 179]. The relatively large differences between simulated and measured adsorption enthalpy for FAU-type zeolites (Table 5.2) suggests that a perfect FAU-type silica structure is not an ideal model for the experimentally used FAU-type zeolites that include non-framework debris left inside their pores by steaming. The good match between simulated and measured adsorption enthalpy for sieves other than FAU-type zeolites indicates that perfect silica structures are a good representation of the other sieves.

Considering the good match between the CBMC-simulated and measured ad-

**Table 5.2:** Adsorption enthalpy for n-C<sub>6</sub>, 22DMB, and 23DMB at low loading as obtained from CBMC simulations and from published measured data

Туре	Source	$\Delta H_{nC6}$	$\Delta H_{22DMB}$	$\Delta H_{23DMB}$
code		(kJ/mol)	(kJ/mol)	(kJ/mol)
AFI	Simulated	-54	-53	-59
AFI	Measured [173–175, 179]	-5564	n.a. <sup>a</sup>	n.a. <sup>a</sup>
MOR	Simulated	-59	-54	-62
MOR	Measured [41, 109, 175, 178, 179]	-6269	$-58^{b}$	$-59^{b}$
BEA	Simulated	-55	-47	-57
BEA	Measured [109]	$-58^{b}$	$-50^{b}$	$-55^{b}$
MTW	Simulated	-70	n.a. <sup>c</sup>	n.a. <sup>c</sup>
MTW	Measured [175]	-7075	n.a. <sup>c</sup>	n.a. <sup>c</sup>
CON	Simulated	-58	n.a. <sup>c</sup>	n.a. <sup>c</sup>
CON	Measured [175]	-6065	n.a. <sup>c</sup>	n.a. <sup>c</sup>
FAU	Simulated	-33	-31	
FAU	Measured [109, 178, 179]	-4450	-41 <sup>b</sup>	-42 <sup>b</sup>

<sup>*a*</sup> The data in ref. [176] were measured at too high a pressure to allow extrapolation to zero loading.

<sup>b</sup> Calculated with formulas 1.5 and 1.6 from data provided in ref. [109].

<sup>c</sup> Not available.

sorption enthalpies at low loading, it is surprising that the CBMC-simulated adsorption data do not reproduce the measured preference for adsorbing 22DMB rather than  $n-C_6$  (Table 5.1). Most notably, the CBMC simulations reproduce neither the lower Gibbs free energy of adsorption nor the lower adsorption enthalpy of branched paraffins as compared to normal paraffins in AFI-type sieves (Table 5.1). Instead, the adsorption enthalpies of branched 22DMB and linear  $n-C_6$  are similar and decrease steadily with pore size, until repulsive interactions with the pore walls increase the adsorption enthalpy of 22DMB relative to that of  $n-C_6$  (Figure 5.2). This is at approximately 0.65 nm as represented by OFF-, CON- and MOR-type silica (Figure 5.2, Table 5.3). The repulsive interactions do not have much of an effect on the adsorption entropy until the fit with 22DMB becomes really tight (as in MTW, VET, SFE, Figure 5.3, Table 5.3). As a result, the Gibbs free energies of both 22DMB and n-C<sub>6</sub> decrease with pore size for as long as there are no repulsive interactions (until GME-, AFI-, CFI-sized pores, Figure 5.4, Table 5.3). Once the walls start to repulse 22DMB (in OFF-, CON-, MOR-sized pores), the Gibbs free energy of adsorption of 22DMB increases significantly relative to that of  $n-C_6$  (Figure 5.4, Table 5.3). Thus, CBMC simulations suggest that 22DMB has a Gibbs free energy of adsorption that is either higher than or approximately equal to that of  $n-C_6$ . As with the adsorption enthalpies, the CBMC-simulated Gibbs free energies calculated at low loading appear not to correlate with the Gibbs free energies of adsorption determined from the measured ternary isotherms (Table 5.1).



**Figure 5.2:** Difference in adsorption enthalpy between 22DMB and  $n-C_6$  as calculated by CBMC. The structures are listed in order of increasing pore size.



**Figure 5.3:** Difference in adsorption entropy between 22DMB and  $n-C_6$  as calculated by CBMC. The structures are listed in order of increasing pore size.

Table 5.3: $(\Delta G_{n-C6}, \Delta S_{22DMB})$	Therm, $\Delta G_{22L}$ , $\Delta G_{22L}$ , $\Delta S_{23L}$	odynamic c <sub>MB</sub> , $\Delta G_{23L}$ <sub>MB</sub> (J/mol	lata on vario MB (kJ/mo K)) for n-C <sub>6</sub>	us structures l)), the adsorp , 22DMB and	calculated by ption enthalpy 23DMB, resp	CBMC at lov ; $(\Delta H_{n-C6}, \Delta$ ectively.	v loading, 53; H22DMB, $\Delta I$	3 K: The Gibb T <sub>23DMB</sub> (kJ/n	s free energy ool)) and entro	of adsorption, ppy, $(\Delta S_{n-C6},$
	pore									
Type	size	$\Delta G_{n-C6}$	$\Delta H_{n-C6}$	$\Delta S_{n-C6}$	$\Delta G_{22DMB}$	$\Delta H_{22DMB}$	$\Delta S_{22DMB}$	$\Delta G_{23DMB}$	$\Delta H_{23DMB}$	$\Delta S_{23DMB}$
Code	(uuu)	(kJ/mol)	(kJ/mol)	(J/mol K)	(kJ/mol)	(kJ/mol)	(J/mol K)	(kJ/mol)	(kJ/mol)	(J/mol K)
FAU	1.20	-14.5	-33.1	-35.0	-14.2	-31.5	-32.4	1	I I	1
LTL	1.00	-16.1	-41.8	-48.1	-15.9	-38.9	-43.3	-20.5	-44.3	-44.7
MEI	0.95	-19.3	-45.9	-49.8	-18.6	-42.8	-45.5	-23.5	-48.0	-45.9
AET	0.83	-18.4	-42.9	-46.0	-19.7	-42.1	-42.0	-24.5	-47.3	-42.8
DON	0.82	-20.2	-44.4	-45.3	-21.3	-43.0	-40.7	1	1	;
AFR	0.77	-18.3	-46.5	-52.9	-20.3	-46.1	-48.3	1	1	;
MAZ	0.74	-18.5	-49.6	-58.5	-19.8	-48.9	-54.7	-25.3	-54.9	-55.5
CFI	0.74	-25.3	-55.8	-57.1	-25.7	-54.6	-54.3	1	1	!
AFI	0.73	-24.5	-54.0	-55.3	-25.4	-52.9	-51.6	-31.4	-59.4	-52.6
GME	0.70	-18.8	-49.0	-56.5	-19.6	-47.6	-52.5	1	1	1
OFF	0.68	-22.1	-56.1	-63.8	-19.1	-52.1	-62.0	1	I I	I I
CON	0.66	-22.2	-57.6	-66.3	-16.8	-51.9	-65.9	1	1	1
MOR	0.64	-23.2	-58.8	-66.7	-17.8	-53.7	-67.2	-24.9	-61.6	-68.9
SSZ-31	0.64	-26.2	-61.1	-65.5	-17.5	-52.7	-65.9	1	1	1
BEA	0.64	-24.3	-55.1	-57.8	-14.1	-46.8	-61.3	-23.8	-56.7	-61.7
SFE	0.64	-22.9	-59.9	-69.3	-11.2	-50.9	-74.6	I I	I I	1
VET	0.59	-25.9	-66.2	-75.5	-12.9	-56.6	-82.0	I I	I I	1
MTW	0.58	-27.2	-69.3	-78.9	-3.9	-49.7	-86.1	1	1	1

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**Figure 5.4:** Difference in Gibbs free energy of adsorption between 22DMB and  $n-C_6$  as calculated by CBMC. The structures are listed in order of increasing pore size.

Adsorption at high loading The incompatibility of simulated adsorption data at low loading and the adsorption data obtained from ternary isotherms suggest that the latter might not be at low loading. To evaluate this important assumption of Santilli et al., the measured ternary adsorption isotherm of an equimolar mixture of 22DMB, 3MP and n-C<sub>6</sub> by AFI-type silica at 403 K was simulated to investigate the loading under experimental conditions. In view of the large variation in measured adsorption selectivity at high to intermediate loading [159, 172], it matches the measured data quite reasonably (Figure 5.5). The simulated isotherm indicates that the measured adsorption data at 14 kPa C<sub>6</sub> were obtained at ~56% of the saturation loading (Figure 5.5). At such a high loading entropic effects due to intermolecular interactions tend to dominate the Gibbs free energy [33, 170, 171]. This would imply that simulations based on an assumption of low loading are largely irrelevant.

The importance of the intermolecular entropy effects appears to scale with pore size. One can distinguish five basic categories:

The first category comprises sieve structures with pores no more than 0.6 nm across (such as TON-, MTT-type zeolites). As discussed elsewhere [87], these sieves repulse paraffins with proximate methyl groups so strongly, that they do not adsorb significant amounts at any pressure, and strongly prefer linear paraffins to branched paraffins.

The second category comprises sieves with pores with a diameter in the 0.60 to 0.70 nm range (such as MOR-, MTW-, SSZ-31-, and BEA-type zeolites). MOR-type zeolites afford a particular nice example (Figure 5.6). At low loading, zeolite-adsorbent interactions dominate, and the isomer with the lowest adsorption enthalpy, n-C<sub>6</sub>, is preferred (Table 5.1, Figure 5.2). At high loading, differences in packing efficiency





**Figure 5.5:** Comparison simulations vs. experiments [159] for a equimolar mixture of 22DMB, 3MP, and  $n-C_6$  in AFI-type silica, T=403 K.

**Figure 5.6:** Simulated adsorption isotherm of an equimolar mixture of 22DMB and n- $C_6$  in MOR-type silica, T=403 K.

change the preference towards branched isomers (Figure 5.6), because these isomers are shorter so that more of them can stack into a single file [77, 180] whilst retaining a larger number of conformations than the straightened-out linear isomers (Figure 5.7).

The third category comprises tubular 0.70-0.75 nm pore structures (AFI-, CFI-, MAZ-, and AFR-type sieves). These have no preference for 22DMB or n-C<sub>6</sub> at low loading (Figure 5.4), but prefer to adsorb the shortest, most branched isomer at high loading (Figure 5.5). A publication that suggested that AFI's preference for 22DMB would already show up at low loading [175] discusses experiments that were done at too high a pressure and too low a temperature ( $10^3$  kPa, 303-333 K, as compared to <<<  $10^3$  kPa, 403 K, Figure 5.5) to actually approach low loading.

The fourth category comprises sieves with pores in the 0.80 nm range (DON- and AET-type sieves). As with the previous two categories, these sieves adsorb  $C_6$  mostly in a single file, but the void volume is now so large that it allows n- $C_6$  to adsorb in many different configurations, from curled-up to stretched nearly perpendicular to the pore axis (Figure 5.7). This allows the number of conformations and the effective length of n- $C_6$  to converge towards that of 22DMB. The preference of adsorbing 22DMB rather than n- $C_6$  decreases accordingly (cf.  $\delta \Delta G_{14kPa22-n}$  in Table 5.1).

The fifth category comprises sieves with pores in the order of 1.0 nm and larger (e.g. FAU-, LTL-, MEI-, VFI-type sieves). These pores accommodate more than a single file of molecules, so that differences in the enthalpy of condensation start to contribute, and  $n-C_6$  becomes preferred over 22DMB because the former has the highest boiling point (Table 5.1).

Remarkably, the differences in Gibbs free energy between 22DMB and n-C<sub>6</sub> calculated from simulated binary isotherms at 14 kPa,  $\delta\Delta G_{14kPa22-n}$  (kJ/mol), correlate



**Figure 5.7:** The top four tubes represent typical conformations of linear and branched C6 isomers adsorbed in AFI (left) and DON (right). In the smaller pore of AFI, the effective size difference between linear and branched isomers is maximized. In the wider pore of DON, the linear isomer can adapt a wider range of conformations, diminishing the entropy effect caused by packing. The bottom tube depicts schematically the experimental conditions, when the pores are fully loaded. Under these conditions entropy effects caused by alkane-alkane interactions become important, driving the isomerisation reaction towards the most compact isomer.

quite well with the differences in Gibbs free energy of adsorption determined from measured ternary isotherms at 14 kPa,  $\delta \Delta G_{14kPa22-n}$  (kJ/mol)(Table 5.1). MTW-type zeolite is the exception. Reasons for the discrepancy between the simulated and experimental data on the MTW-type zeolite include exterior surface effects and a high sensitivity of the modeling parameters to tightly fitting molecules [87]. The close similarity of data obtained from measured and simulated isotherms indicates that the relative preference of structures for adsorbing the shorter 22DMB rather than the longer n-C<sub>6</sub> predominantly reflects a difference in adsorption entropy (packing efficiency) peculiar to adsorption in a one dimensional pore. As this type of adsorption entropy is a result of intermolecular interactions, it does not become apparent until relatively high loading. It now remains to be sorted out how the adsorption entropy found at high loading can affect shape selectivity.

**Catalysis: Paraffin Hydroconversion Mechanism** Before addressing how structures can affect the paraffin hydroconversion selectivity of both complex industrial feeds [169] and n-C<sub>16</sub>, [158, 159] it is useful to discuss the current model for paraffin hydroconversion. The hydroconversion of linear paraffins consists of a series of consecutive hydroisomerization reactions that steadily increase the degree of branching. Although all hydroisomerization reactions strive towards chemical equilibrium, equilibrium is never achieved due to an increasing chance of irreversible hydrocracking reactions with increasing degree of branching [16]. When long paraffins like n-C<sub>16</sub> hydrocrack early in the chain of hydroisomerization reactions they yield n-C<sub>6</sub> when they hydrocrack late, they yield DMB [21,181]. Therefore, the ratio between the

initially formed DMB and n-C<sub>6</sub> is a measure for the extent to which n-C<sub>16</sub> hydroisomerizes before it hydrocracks, and thereby, for the rate of the hydroisomerization reactions relative to that of the hydrocracking reactions. In practice, measuring the ratio between initially formed DMB and n-C<sub>6</sub> is impeded by consecutive hydroisomerization reactions that drive the initially produced C<sub>6</sub> fraction towards its intracrystalline thermodynamic equilibrium [77]. Extensive consecutive hydroisomerization reactions are likely at the ~99% n-C<sub>16</sub> hydroconversion at which Santilli et al. report their data.

**Catalysis: Impact of C**<sub>16</sub> Adsorption Thermodynamics Santilli et al. attributed the variation of the branching hydroisomerization rate with zeolite structure (Figure 5.1) to a variation in the stabilization of the transition state for forming branched  $C_{16}$  paraffins [158, 159]. Such a kinetic explanation for differences in hydroisomerization rate was favored, because it was assumed that the paraffins inside molecular sieves would all approach the same (gas phase) equilibrium [158, 159]. In addition, the computational techniques available in the early 1990s did not allow Santilli et al. to perform the calculations for the systems of interest (long chain hydrocarbons), at the conditions of interest (high pressure). To make the computations feasible they had to assume that the behavior of the short chain paraffins at infinite dilution is representative. Nowadays, long chain hydrocarbons at reaction conditions are amenable to molecular simulations, as illustrated by the simulated binary isotherm of equal amounts of 2,5,8,11-tetramethyldodecane (a teMe- $C_{12}$ ) and n- $C_{16}$  at 577 K (Figure 5.8). It shows that AFI- and DON-type pores are fully saturated with reactant under reaction conditions ( $3x10^3$  kPa C<sub>16</sub>, 577 K [159]). Similar simulations show that also pores as large as the 1.2 nm wide FAU-type supercages are fully saturated with reactant under these conditions. When pores are at saturation loading, molecular exchange between gas phase and adsorbed phase will be too slow to bring the adsorbed phase to gas phase chemical equilibrium [16, 124, 165, 166]. Instead, the adsorbed phase will exhibit an intracrystalline chemical equilibrium as defined by the intracrystalline Gibbs free energies of formation of the various isomers [77, 88]. The intracrystalline chemical equilibrium tends to favor the formation isomers with the lowest Gibbs free energy of adsorption [77, 88], because isomers of the same carbon number usually have a comparable Gibbs free energy of formation in the gas phase [22]. Therefore the lowest Gibbs free energy of adsorption tends to correspond to the lowest Gibbs free energy of formation in the adsorbed phase [77, 88, 89].

The binary isotherms indicate that AFI- and DON-type zeolites equally prefer adsorbing and forming branched rather than linear  $C_{16}$  under reaction conditions (577 K, 3x10<sup>3</sup> kPa, Figure 5.8). n- $C_{16}$  is that much longer than n- $C_6$  that it cannot curl up or re-orient itself the way n- $C_6$  can in DON-type pores, and thereby reduce its effective length. n- $C_{16}$  inside DON-type pores remains stretched out, to the extent that its length approaches that of n- $C_{16}$  in a AFI-type pore. With the disappearance of differences in effective length of the n-paraffin, also the difference in preference between DON- and AFI-type pores for branched rather than linear paraffins vanishes when going from  $C_6$  to  $C_{16}$ .

Our simulations clearly indicate that none of the key assumptions underlying the mechanism of inverse shape selectivity hold. The pores are not nearly empty, but



**Figure 5.8:** Simulated adsorption isotherms (577 K) of an equimolar mixture of 2,5,8,11-teMe- $C_{12}$  and n- $C_{16}$  in AFI- and DON-type silica.

saturated with reactant under reaction conditions. The hydroisomerization reactions do not approach gas phase but adsorbed phase chemical equilibrium. One cannot extrapolate the thermodynamic stabilization of adsorbed branched  $C_6$  isomers to that of adsorbed branched  $C_{16}$  isomers.

**Catalysis: Impact of C**<sub>6</sub> **Adsorption Thermodynamics** An alternative mechanism can be formulated if one assumes that the C<sub>6</sub> hydrocracking products formed initially will continue to hydroisomerize as long as more slowly diffusing C<sub>16</sub> molecules keep them trapped inside the pores. As long as it remains trapped, C<sub>6</sub> will hydroisomerize towards the chemical equilibrium inside the pores. Once desorbed, C<sub>6</sub> will fail to compete with C<sub>16</sub> for re-adsorption, so that the C<sub>6</sub> isomers will not continue to hydroisomerize to reach a gas phase chemical equilibrium distribution (Figure 5.8). Although Santilli et al. assumed that C<sub>6</sub> hydroisomerization would be negligible [159], we would expect extensive C<sub>6</sub> hydroisomerization, for the reaction temperature is 577 K [159], which is significantly above the threshold temperature for C<sub>6</sub> hydroisomerization. Typically these reactions are carried out at 520 K or higher [182,183].

Santilli et al. argued that the 9 times higher yield of 23DMB as compared to 22DMB is far from gas-phase chemical equilibrium and that, therefore, consecutive  $C_6$  hydroisomerization was precluded [159]. We would argue that the high 23DMB yield does not preclude consecutive  $C_6$  hydroisomerization, because 23DMB is kinetically favored to 22DMB [184], and so is the first DMB to form. At the high hydrocarbon pressure used [159], 23DMB is also thermodynamically favored to 22DMB. This thermodynamic preference is in agreement with the majority of the adsorption data [159, 172]. The lower Gibbs free energy of formation and adsorption of 23DMB relates to a smaller loss of entropy upon adsorption, because the vicinal methyl groups in 23DMB allow for a larger number of conformations than the gemi-

nal methyl groups in 22DMB. Because of its entropic origin, the intracrystalline thermodynamic driver for 23DMB rather than 22DMB at the conditions of simulation  $(5x10^2 \text{ kPa}, 403 \text{ K})$  will be even higher at the higher pressure and temperature under reaction conditions  $(3x10^3 \text{ kPa} \text{ hydrocarbon}, 577 \text{ K})$ . By contrast, gas phase thermodynamics would drive towards 22DMB rather than 23DMB formation [22, 184]. Thus, the predominance of 23DMB in the DMB fraction corroborates that intracrystalline thermodynamics drives the hydroisomerization reactions of the hydrocracking products towards the compound with the lowest intracrystalline Gibbs free energy of formation.

The strongest support for the predominant influence of the intracrystalline chemical thermodynamics on the  $C_6$  yield structure is that the simulated adsorption thermodynamics affords a quantitative link between the C<sub>6</sub> adsorption thermodynamics and the  $C_6$  yield structure in n- $C_{16}$  hydroconversion (Table 5.4, Figure 5.9). With the assumption that for all catalysts the  $C_6$  hydroisomerization proceeds to a comparable percentage of their respective intracrystalline chemical equilibrium,  $\delta\Delta G_{catal}$ (kJ/mol) should represent the difference in free energy of formation between 22DMB or 23DMB and  $n-C_6$  inside the sieves. It turns out, that there is a linear relationship between this difference in Gibbs free energy of formation and the simulated differences in Gibbs free energy of adsorption (either at adsorption conditions (14 kPa, 403 K) or at reaction conditions (3x10<sup>3</sup> kPa, 577 K)). The deviation of the CFI-type zeolite sample from this Gibbs free energy correlation is probably related to the exceptionally high temperature required to achieve 70% hydrocracking activity on the single CFI-type sample that has been evaluated [185, 186]. If CFI is excluded, the variation in the differences in free energy of adsorption between DMB and n-C<sub>6</sub> explains 90% of the variation in the differences in the free energy of formation (i.e. the correlation coefficient is 0.90). This linear correlation between the free energy of formation and of adsorption of DMB and n-C<sub>6</sub> is illustrated by a good match between the DMB/n-C<sub>6</sub> yield and simulated adsorption ratios in the traditional bell-shaped curve in Figure 5.9. The measured differences in free energy of adsorption at 14 kPa follow pretty much the same correlation as the simulated values at saturation loading (Table 5.4). The good correlation between the differences in the Gibbs free energy of adsorption and of formation of  $C_6$  isomers corroborates the suggestion that the intracrystalline thermodynamic equilibrium determines the direction of the hydroisomerization of the  $C_6$  isomers that are formed initially in n- $C_{16}$  hydroconversion.

In chapter 4, we have shown how pores selectively adsorb and produce molecules to the extent that they have a shape commensurate with that of the pore [87–89]. When the shapes are more commensurate, Van der Waals interaction between the pore walls and the adsorbate decrease the adsorption enthalpy and, thereby, the Gibbs free energy of adsorption and formation. It has now been found that pores can also favor the adsorption and formation of molecules because they are more compact, lose less entropy upon adsorption, and, thereby, have a lower Gibbs free energy of adsorption and formation.

The shape selective redirection of the hydrosomerization reactions commensurate with the adsorption-induced shift in the Gibbs free energy of formation of reactants and products is a novel form of shape selectivity. This shape selective change in reac-

	13000kPa23-n	(s)/ III01/ are	ule samle par e		, UAIU NI a.		
Void	Structure	$\delta\Delta G_{catal}$	$\delta \Delta G_{ads22-n}$	$\delta \Delta G_{500kPa22-n}$	$\delta\Delta G_{500kPa23-n}$	$\delta\Delta G_{3000kPa22-n}$	$\delta\Delta G_{3000kPa23-n}$
Category	Code	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
V 0.9-1.0 nm	LTL	8.6	3.9	7.1	0.8	3.2	-1.8
V 0.9-1.0 nm	MEI	n.aa	n.a.	6.3	2.6	;	1
V 0.9-1.0 nm	FAU	10.0	1.3	4.0	-1.8	1.0	-3.2
IV 0.8 nm	DON	7.6	n.a.	2.5	-4.2	-2.8	-8.1
IV 0.8 nm	AET	n.a.	n.a.	0.3	-4.9		
III 0.70-0.75 nm	MAZ	-0.4	n.a.	-8.4	-14.9	-6.3	-13.4
III 0.70-0.75 nm	AFI	0.2	-4.8	-8.0	-16.0	-6.5	-14.2
III 0.70-0.75 nm	CFI	5.3	n.a.	-5.6	-17.3		1
III 0.70-0.75 nm	AFR	n.a.	n.a.	-2.9	-8.1		1
II 0.60-0.70 nm	MOR	2.6	-0.9	-2.2	-10.6	0.2	-7.4
II 0.60-0.70 nm	SSZ-31	4.9	n.a.	1.6	-9.8	4.6	-8.9
II 0.60-0.70 nm	BEA	6.0	з.5	3.5	-6.4	6.5	-3.7
II 0.60-0.70 nm	MTW	12.1	7.2	12.5	-1.7	19.3	3.5

of adsorption between 22DMB or 23DMB and n-C6 d (k]/mol) and $\delta \Delta G_{3000kPa23-n}$ (k]/mol) are the same	ternary isotherm, at 403 K and 14 kPa C6; $\delta \Delta G_{500kPa}$	K [159], $\delta \Delta G_{ads22-n}$ (kJ/mol) is the difference in Gibt	Table 5.4: $\delta \Delta G_{catal}$ (kJ/mol) corresponds to the dif	
B or 23DMB and n-C6 determined from a simulated binary isotherm at 403 K and 500 kPa, $\delta \Delta G_{3000kP}$ $_n$ (kJ/mol) are the same but determined at 577 K, 3x10 <sup>3</sup> kPa.	d 14 kPa C6; $\delta \Delta G_{500kPa22-n}$ (kJ/mol) and $\delta \Delta G_{500kPa23-n}$ (kJ/mol) are the differences in Gibbs free e	) is the difference in Gibbs free energy of adsorption between 22DMB and n-C6 determined from a mea	) corresponds to the difference in Gibbs free energy of formation between teMe- $C_{12}$ and diMe- $C_{14}$	
-n	gy	ed	577	



**Figure 5.9:** Experimental and simulated DMB/n-C<sub>6</sub> normalized yield ratios (y) for various zeolite structures at T = 577 K and P = 3000 kPa. The ratios were normalized with respect to the FAU-type zeolite. The experimental ratios (red  $\blacktriangle$ ) were taken from n-C<sub>16</sub> hydroconversion experiments, [159, 185], the calculated ratios were taken from simulated adsorption isotherms of equimolar mixtures of 22DMB/n-C<sub>6</sub> (yellow  $\blacksquare$ ) and 23DMB/n-C<sub>6</sub> (blue  $\blacklozenge$ ) or from simulated Henry coefficients (green  $\bullet$ ). The numbers in parentheses are the average pore sizes (Å).

tion kinetics is not a form of transition state shape selectivity, for it does not require an alteration of the Gibbs free energy of formation of any transition state or intermediate. Indeed a change in the Gibbs free energy of formation of a transition state is difficult to envisage, given the entropic origin of the free energy changes. In the light of the above analysis, the term "inverse shape selectivity" loses much of its relevance. Inverse shape selectivity was defined as the selective acceleration of the formation of bulky products, so as to contrast with regular shape selectivity, which was defined as the selective deceleration of the formation of bulky products [158]. We would argue that the compatibility between adsorbate and adsorbent defines what are bulky and what are compact molecules. DMB is more bulky than n-C<sub>6</sub> in highly constrained MTW-type pores (reflected by DMB's higher adsorption enthalpy), whereas the inverse is true for AFI-like pores at high pressure (reflected by DMB's lower adsorption entropy). According to this definition, the preference of MTW-zeolites for adsorbing and forming n-C<sub>6</sub> rather than DMB and the inverse preference of AFI-like zeolites both are examples or regular - not inverse - shape selectivity.

In our mechanism the role of the zeolite is to provide an environment in which the length differences between the linear and branched isomers are at its maximum, which translates into an optimal pore diameter. For a given pressure, the maximum selectivity is determined by the relative effective sizes of the alkane molecules. The details of the channel structure are in this mechanism of secondary importance. This suggests that we can "optimise" any zeolite structure by tuning its diameter. In Fig-



**Figure 5.10:** Normalized 2,2-DMB/n-C<sub>6</sub> yield ratios (with respect to the FAU selectivity) for some "optimized"1 pore systems at T=403 K and P=1000 kPa. The size of MOR- (circle, pore too small), AFI- (square, optimal), AET- (diamond, too wide), and DON-type (triagle, too wide) channels was adjusted by scaling the coordinates. The open symbols represent the zeolite structures before resizing. MOR was first made circular efore the scaling was applied.

ure 5.10 we have performed this optimisation for several known zeolite structures by changing the pore diameters by a simple scaling factor. Of course, such an optimisation cannot be performed in practice, but does illustrate our point that irrespective of the details of the zeolite a similar optimal selectivity is obtained for nearly identical channel dimensions. At lower temperatures or higher pressures the entropy effect is more pronounced and a better selectivity could be expected. The results in Figure 5.10 are at lower temperatures compared to the results in figure 1 (403 K versus 577K). The data at these lower temperatures give significantly higher selectivities. A similar effect can be expected from an increase of the pressure.

### 5.2 Conclusions

Molecular simulations show that differences in the Gibbs free energy of adsorption explain differences in paraffin hydroisomerization selectivity between catalysts. The important aspect of this work is that this selectivity can only be explained if we consider the zeolite to be fully saturated with reacting molecules. These saturated pores trap paraffins long enough to allow them to equilibrate towards the intracrystalline chemical equilibrium distribution. Pores less than 0.70 nm across equilibrate less towards branched paraffins than larger pores, because they repulse branched paraffins causing an increase in enthalpy of formation. This increase offsets their higher entropy of formation as a result of their better stacking efficiency. Pores 0.70-0.75 nm

#### 5.2 Conclusions

across are optimal for forming branched rather than linear paraffins, because they are large enough not to repulse the branched paraffins, and thereby, maximize the effect of the better stacking efficiency of the shorter, branched paraffins. In larger pores linear  $C_6$  paraffins can curl up, so that the differences in stacking efficiency between branched and linear paraffins disappear. This effect is markedly reduced for  $C_{16}$  paraffins. When pores approach 1.0 nm, condensation effects start to add in, and further reduce the preference for lower-boiling branched isomers instead of higher-boiling linear isomers. These entropy (stacking) effects only occur at high loadings, in which adsorbate-adsorbate interactions are important. This thermodynamic explanation for the high branched-paraffin yield in  $n-C_{16}$  hydroconversion is more rigorous than earlier explanations invoking (inverse) transition state shape selectivity involving adsorbate zeolite interactions only. The link between adsorption thermodynamics and catalytic activity is well established [123,161,162,187–190]. The link between the Gibbs free energy of adsorption and shape selectivity has also been observed before [88, 89], but only with respect to a lower adsorption enthalpy when molecular and pore shapes are commensurate. To the best of our knowledge, this is the first instance of shape selective adsorption and production that is due to higher (i.e. less negative) adsorption entropy and a concomitantly lower Gibbs free energy of formation in the adsorbed phase. It is probably not the last instance, for e.g. kinetic data on aromatics hydroconversion [191, 192] also seem to indicate that adsorption entropy may play a significant role in the selectivity in these types of conversions. Clearly adsorption entropy not only affects the activity [123, 189, 190], but also the selectivity of many zeolite catalyzed conversions.

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## Summary

The subject of this thesis is the shape selective processing of alkanes by zeolites. In this study we try to understand the intrinsic differences in adsorption, diffusion, and catalytic behavior between various zeolite topologies in alkane processing. The approach is to link the shape selectivity observed in processes like hydroconversion and alkane separation to adsorption thermodynamics. The thermodynamic data needed for such an assessment are not always readily amenable to experiments, therefore this data is obtain by computer simulation.

Chapter 1 provides a short introduction to zeolites, alkane processing with zeolites, and the applied computer simulation techniques.

In chapter 2, we validate the forcefields used to model the alkanes and the zeolitealkane interactions. The forcefields were developed using low pressure data of linear and branched alkanes adsorbed in MFI. As such, they are capable of reproducing Henry coefficients, heats of adsorption and adsorption isotherms of linear and branched alkanes in MFI over a wide range of temperatures. In this chapter it is found that the same forcefields are also capable of reproducing experimental data in other zeolites. Additionally, in the last section, we verify the assumption that the zeolite can be modeled as a rigid crystal in the case of adsorption experiments. For this, Henry coefficients, heats of adsorption, and adsorption isotherms of linear and branched alkanes in MFI are calculated using a variable flexibility of the zeolite framework. We find that at low loading, the influence of the framework flexibility on the heat of adsorption and Henry coefficient is quite small. On the other hand, for molecules with an inflection behavior such as isobutane and heptane, the influence at high loading seems to be much larger.

In chapter 3, we discuss the adsorption of alkanes and their mixtures at high pressures. In this regime entropy effects induced by intermolecular interactions come into play that affect the adsorption considerably. In the first part of the chapter the various entropy, or packing, effects are discussed: Configurational entropy comes into play when there is a large difference in the number and energetics of adsorption sites between different molecules. Length entropy effects come into play in uni-dimensional pore systems where the most compact molecule has highest packing efficiency. These entropy effects are subsequently used in the second part of the chapter to study the separation of alkane isomers using Silicalite-1.

Chapter 4 focuses on differences between zeolite topologies in shape selective alkane hydroconversions at low pressures. It starts with a concise description of traditional concepts in shape selectivity and how these can be identified using adsorption thermodynamics. This methodology is subsequently used to analyze three test cases: (1) The use of TON-, MTT- and AEL-type zeolites in the de-waxing of long n-paraffins. (2) The difference in cracking performance between two similar zeolites MFI and MEL. (3) The effect of commensurability of 2,x-dimethylpentadecanes on the diffusion and conversion in TON. In case (1) it is found that the high selectivity of these zeolites towards hydroisomerization instead of hydrocracking can be explained by their ability to suppress the formation of paraffins with neighboring methyl groups. In case (2) it is found that the large difference in yield of iso-butane between MFI and MEL during decane hydrocracking can be explained by the formation of different reaction intermediates, commensurate with the channel intersections of both zeolites. In case (3) it is found that the spacing between two methyl groups of dimethylpentadecanes has a large influence on the diffusion of these molecules. If the methyl-spacing is such that the molecule is commensurate with the undulations in the TON-pore, the diffusion slows down considerably. This has also implications for the catalytic selectivity.

In chapter 5, the study of the differences between zeolite topologies in shape selective alkane hydroconversions is extended to high pressures. The entropy effects introduced in chapter 3 are used to explain differences in product distribution between various large pore zeolites in hexadecane hydroconversion. This conversion serves as a model reaction for the production of gasoline from crude oil, in which the yield of dimethylbutanes has to be maximized. It is found that the entropy effects are maximized in zeolites with a pore diameter of approximately 7.5 Å. As a result these zeolites produce the highest percentage of dimethylbutanes.

## Samenvatting

Dit proefschrift gaat over het vormselectief verwerken van alkanen door zeolieten. In deze studie proberen we het effect van de zeolietstructuur op het adsorptie- en diffusiegedrag van alkanen alsmede het effect op het katalytisch converteren van alkanen te begrijpen. Hiervoor vertalen wij begrippen en observaties uit de zeolietliteratuur naar adsorptiethermodynamica. De thermodynamische data die nodig zijn om de analyses te maken kunnen niet altijd eenvoudig uit experimenten gehaald worden. Daarom maken wij gebruik van computer simulaties om deze data te verkrijgen.

Hoofdstuk 1 geeft een korte inleiding over zeolieten, het verwerken van alkanen met behulp van zeolieten, en de gebruikte computationele technieken.

In hoofstuk 2 testen we de modellen die de alkanen en de interacties tussen de alkanen en de zeolieten beschrijven. Deze modellen zijn ontwikkeld met behulp van experimentele data over de adsorptie van lineaire en vertakte alkanen in het zeoliet MFI by lage druk. Deze modellen zijn goed in staat om Henry-coefficienten, adsorptiewarmtes en adsorptie-isothermen van lineaire en vertakte alkanen in MFI bij uiteenlopende temperaturen te reproduceren. In dit hoofdstuk stellen we vast dat deze modellen ook in staat zijn om experimentele data in andere zeolieten te reproduceren. In het laatste deel van het hoofdstuk verifieren we of de aanname dat een zeoliet als een rigide kristal beschouwd kan worden juist is. Hiervoor rekenen we Henry-coefficienten, adsorptiewarmtes en adsorptie-isothermen van lineaire en vertakte alkanen uit als functie van de flexibilteit van het kristalrooster. We vinden dat bij lage belading de invloed van de flexibiliteit op de adorptiewarmte en de Henrycoefficient vrij klein is. Voor moleculen met inflectiegedrag, zoals isobutaan en heptaan, geldt dat de invloed bij hoge belading veel groter is.

In hoofdstuk 3 bestuderen wij de adsorptie van alkanen en mengsels van alkanen bij hoge druk. Bij hoge druk gaan de moleculen elkaar voelen, wat resulteert in allerlei entropie-effecten. Deze entropie-effecten blijken een belangrijke stempel te drukken op het adsorptiegedrag van de alkanen, en met name van mengels. In het eerste deel van het hoofdstuk behandelen we verschillende soorten entropie-effecten: configurationele entropie komt voor wanneer er een groot verschil is tussen het aantal en de energie van adsorptieplekken tussen verschillende moleculen. Lengte entropie effecten komen voor in een-dimensionale poriesystemen waar de hoogste pakkingsgraad wordt behaald met behulp van het meest compacte molecuul. De entropieeffecten worden in het tweede deel van het hoofdstuk gebruikt voor het bestuderen van de scheiding van alkaanisomeren met behulp van Silicalite-1.

Hoofdstuk 4 gaat in op de verschillen tussen zeolietstructuren in het vormselectief converteren van alkanen bij lage druk. Het begin van het hoofdstuk behandelt veel gebruikte concepten over de vormselectiviteit en hoe deze zijn te analyseren met behulp van adsorptiethermodynamica. Deze methode wordt vervolgens toegepast op drie onderwerpen: (1) Het gebruik van TON-, MTT-, en AEL-type zeolieten voor het ontwaxen van lange n-alkanen. (2) De verschillen in kraakselectiviteit tussen twee zeolieten, MFI and MEL, die een vergelijkbaar poriesysteem hebben. (3) Het effect van gelijkvormigheid met het poriesysteem van 2,x-dimethylpentadecanes op hun diffusie en omzetting in TON. Wij vinden bij (1) dat de hoge selectiviteit van deze zeolieten voor hydro-isomerisatie in plaats van hydrokraken verklaard kan worden door de onderdrukking van de vorming van alkanen met methylgroepen die dicht bij elkaar liggen. Bij (2) vinden we dat de verschillen in de verhouding isobutaan/butaan, geproduceerd tijdens het kraken van decaan, verklaard kan worden door de vorming van verschillende reactie-intermediairen. Deze intermediairen zijn gelijkvormig met de intersecties van de zeolieten. Bij (3) vinden we dat de afstand tussen de twee methylgroepen bij dimethylpentadecanen een grote invloed heeft op de diffusie van deze moleculen in de TON porien. Als de afstand zodanig is dat het molecuul gelijkvormig wordt met de porie dan gaat de diffussie van deze moleculen flink omlaag. Dit heeft ook grote invloed op de conversie van deze moleculen.

In hoofdstuk 5 wordt de studie naar de verschillen tussen zeolietstructuren in het vormselectief converteren van alkanen uitgebreid naar hogere drukken. De entropieeffecten die in hoofdstuk 3 zijn geintroduceerd worden gebruikt om de verschillen in de productverdeling tussen verschillende zeolieten met grote porien tijdens het converteren van hexadecaan te verklaren. Deze reactie fungeert als een model reactie voor de productie van benzine uit olie, waarbij de opbrengst van dimethylbutanen zo hoog mogelijk moet zijn. We vinden dat de entropie-effecten gemaximaliseerd worden in zeolieten met een poriediameter van ongeveer 7.5 Å. Dit resulteert in de hoogste opbrengst aan dimethylbutanen bij deze zeolieten.

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