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Molecular Simulation

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713644482>

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Simon P. Bates^{ab}; Willy J. M. Van Well^a; Rutger A. Van Santen^a; Berend Smit^{cd}

^a Schuit Institute of Catalysis Laboratory for Inorganic Chemistry & Catalysis, Eindhoven University of Technology, MB Eindhoven, The Netherlands ^b Physics Dept, Keele University, UK ^c Shell International Oil Products, B. V. Shell Research and Technology Centre, Amsterdam, BN, The Netherlands ^d Department of Chem. Eng., Universiteit Van Amsterdam, Amsterdam, WV, The Netherlands

To cite this Article Bates, Simon P. , Van Well, Willy J. M. , Van Santen, Rutger A. and Smit, Berend(1997) 'Configurational-Bias Monte Carlo (CB-MC) Calculations of *n*-Alkane Sorption in Zeolites Rho and Fer', Molecular Simulation, 19: 5, 301 – 318

To link to this Article: DOI: 10.1080/08927029708024159

URL: <http://dx.doi.org/10.1080/08927029708024159>

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CONFIGURATIONAL-BIAS MONTE CARLO (CB-MC) CALCULATIONS OF *n*-ALKANE SORPTION IN ZEOLITES RHO AND FER

SIMON P. BATES^{a,c}, WILLY J. M. VAN WELL^a, RUTGER
A. VAN SANTEN^a and BEREND SMIT^{b,d}

^a*Schuit Institute of Catalysis, Laboratory for Inorganic Chemistry & Catalysis,
Eindhoven University of Technology, P O Box 513, 5600 MB Eindhoven, The
Netherlands;* ^b*Shell International Oil Products, B. V. Shell Research and Technology
Centre, Amsterdam, P.O. Box 38000, 1030 BN Amsterdam, The Netherlands;*

^c*Physics Dept. Keele University, Staffs ST5 5BG, UK;* ^d*Department of
Chem. Eng., Universiteit Van Amsterdam, Nieuwe Achtergracht 166, 1018
WV Amsterdam, The Netherlands*

(Received July 1996; Accepted August 1996)

A newly-developed Monte Carlo method is used to simulate the energetics, location and conformation of *n*-alkanes from butane to decane inside all-silica polymorphs of zeolites rho and ferrierite. Sorption in ferrierite yields far larger heats of adsorption than in rho. In rho, the alkanes adopt highly coiled conformations within the α -cages of the structure, whereas in ferrierite they are confined to all-*trans* conformations within the 10-ring channel. Only butane is distributed over both the 8-ring and 10-ring channels of ferrierite in the approximate ratio of 1 : 2. An increase in temperature to 498 K has little effect on the heats of adsorption, locations or conformations of the alkanes.

Keywords: Monte carlo; simulations; zeolites, *n*-alkanes

INTRODUCTION

Theoretical simulations that employ classical forcefields to describe atomic interactions have become increasingly common in recent years, as rapid hardware and software advances have made this type of investigation more readily accessible to more researchers. Some of the most intense activity in this area has been directed towards the simulation of guest molecules within the pores of microporous hosts, a fact that reflects the commercial importance of such materials [1].

In this paper, we present results of simulations using a novel Monte Carlo (MC) method that we have applied to the study of *n*-alkane adsorption within the pores of the all-silica polymorphs of zeolites ferrierite and rho. This novel MC method – Configurational-Bias Monte Carlo (CB-MC) – has recently been developed for the simulation of chain molecules in a computationally efficient manner. The principles and details of the technique are described in the Appendix, but here we illustrate the efficiency of the method when used to study the sorption of *n*-decane in silicalite, the all-silica polymorph of ZSM-5. The simulation took around 24 hours on a Silicon Graphics Iris 4D/35 workstation [2]; a corresponding experimental study of *n*-decane sorption needed 2 weeks to equilibrate [3] and had Molecular Dynamics methods been used to study this system, it is estimated that the calculation it would take thousands of hours of supercomputer time. The disadvantage that only ‘static’ (rather than ‘dynamic’) information is available from our CB-MC calculations is more than compensated for by the wider range of catalytically-interesting sorbates that may be routinely investigated as a result of this computational efficiency. Indeed, a CB-MC method has been used to investigate the sorption of *n*-alkanes as long as C₄₈H₉₈ in zeolites [4].

We restrict our interest to the zeolites rho and ferrierite, both catalytically important materials. Ferrierite has been found to be a remarkably selective isomerisation catalyst for the conversion of 1-butene to *iso*-butene [5]. The *iso*-butene is then combined with methanol in another acid-catalysed reaction to produce methyl tertiary butyl ether (MTBE), an octane blending agent that can be added to fuel in place of lead. Zeolite rho has been reported as an efficient catalyst for the reaction of methanol and ammonia to selectively produce dimethylamine [6] and also (in its cadmium ion-exchanged state) to encapsulate the highest amount of hydrogen per gram of zeolite at 1 atm that has ever been observed [7].

In addition to their industrial importance, they are structurally contrasting materials. Ferrierite is a zeolite that contains 2 intersecting straight channels; an elliptical channel (5.4 by 4.2 Å) parallel to the [001] crystallographic direction, comprising windows with 10 oxygen atoms (‘10-rings’) and a smaller elliptical 8-ring channel (4.8 by 3.5 Å) parallel to [010]. The structure of zeolite rho consists of α -cages (truncated cuboctahedra) linked via double-eight rings. Access to the voids within the α -cages is provided via narrow, circular 8-ring windows of 3.6 Å diameter. The structures of rho and ferrierite are shown in Figure 1. It is these different pore topologies that are primarily responsible for the contrasting behaviour of the sorbed molecules in the two zeolites, as we show in the next section.

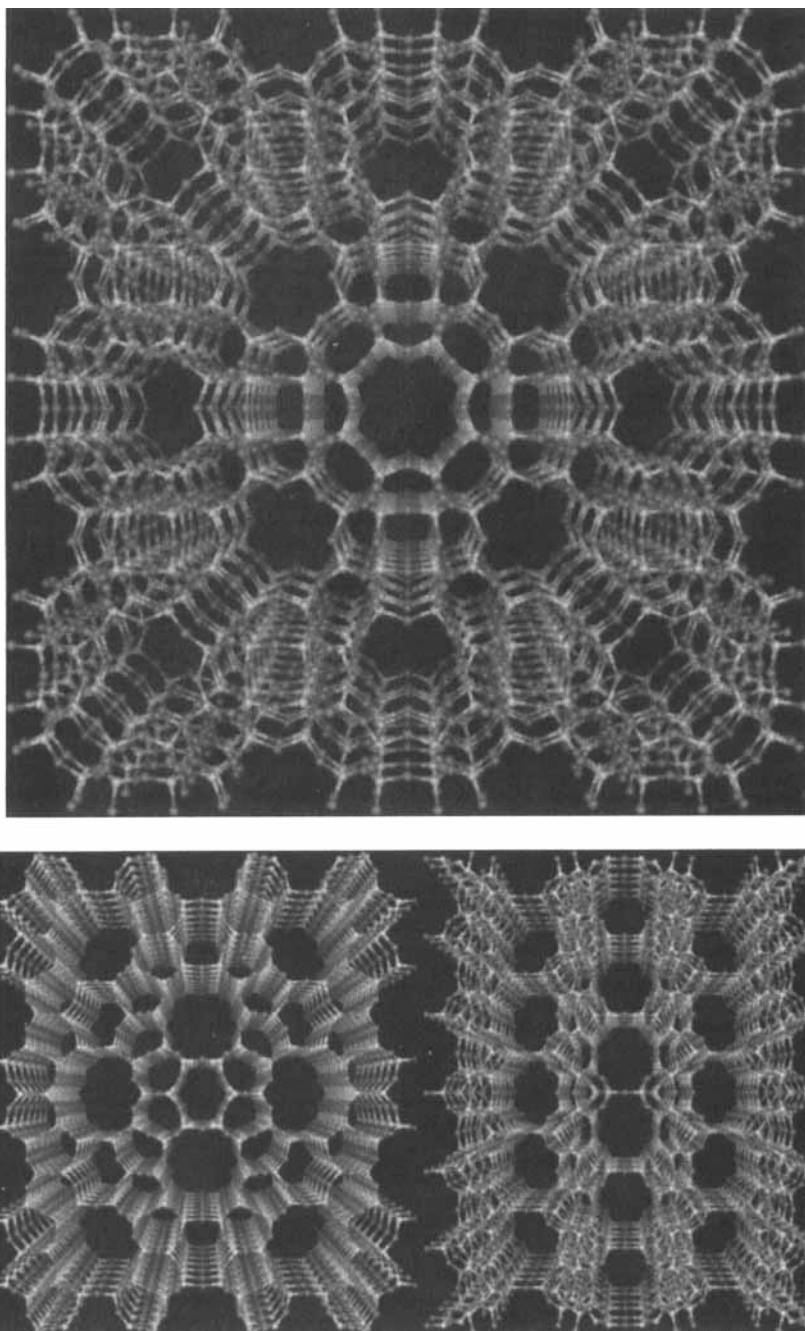


FIGURE 1 Perspective views of zeolites used in simulations: (a) Zeolite rho viewed down one of the three crystallographically equivalent axes: (b) Zeolite ferrierite viewed down the z-axis [001], the direction of the larger 10-ring channel: (c) Zeolite ferrierite viewed down the y-axis [010], the direction of the smaller 8-ring channel (See Color Plate I).

Our simulations (as detailed in the Appendix) provide information on the energetics and location of sorption, together with a profile of the conformation of the sorbed molecule. In the following section, we use the numerical data, pictures and animations that we have obtained from the simulations to illuminate aspects of alkane sorption within these two zeolites.

RESULTS AND DISCUSSION

Energetics of Sorption

Preliminary results of the sorption energetics of *n*-alkanes in rho and ferrierite have been published by us elsewhere [8]. Here, we briefly summarise our findings. Heats of adsorption as a function of carbon number are presented graphically in Figure 2. Whilst both zeolites do stabilise the alkanes (heats of adsorption are exothermic) this stabilisation is far greater in ferrierite than in rho. A similar pattern is seen in the Henry coefficients as a function of carbon number, shown in Figure 3. Numerical data is presented in Table I.

The heat of adsorption of a given alkane is likely to be primarily determined by the pore topology of the framework in which it adsorbs. It is widely accepted that larger zeolite pores, with smaller curvatures, stabilise a given molecule less than those with smaller pores. Indeed, this is supported

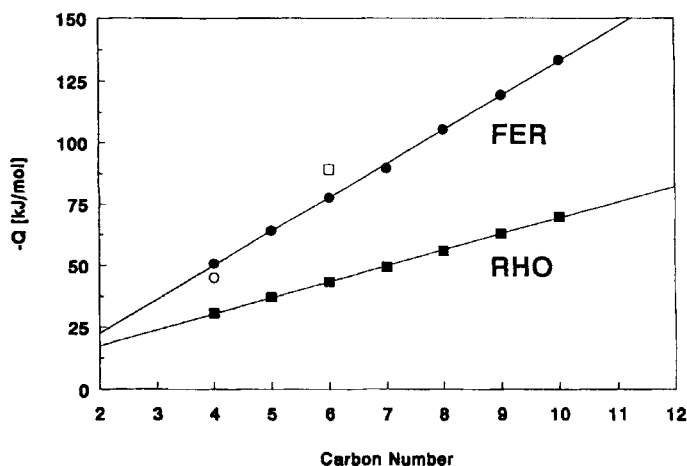


FIGURE 2 Heat of adsorption $[-Q]$ as a function of carbon number for adsorption of *n*-alkane sorption in rho and ferrierite. (The experimental data is for butane in rho [13] and hexane in ferrierite [14]).

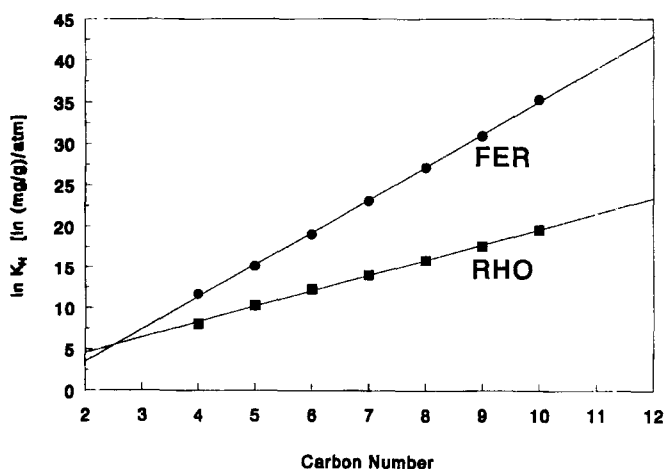


FIGURE 3 Henry coefficient [K_H] as a function of carbon number for adsorption of n -alkane sorption in rho and ferrierite.

TABLE I Heat of adsorption, Q , and Henry coefficient, K_H values for alkanes in all-silica rho and ferrierite

Zeolite Code	Alkane chain length	Q [kJ/mol]	$\ln K_H$ [ln(mg/g)/atm]
RHO	C ₄	-30.5	8.07
	C ₅	-37.1	10.30
	C ₆	-43.3	12.28
	C ₇	-49.3	14.06
	C ₈	-55.8	15.85
	C ₉	-62.7	17.58
FER	C ₁₀	-69.7	19.60
	C ₄	-50.7	11.70
	C ₅	-64.0	15.15
	C ₆	-77.6	19.07
	C ₇	-89.7	23.10
	C ₈	-105.4	27.12
	C ₉	-119.3	30.92
	C ₁₀	-133.3	35.29

by experimental measurements on the heat of adsorption in zeolites of different pore sizes [9]. Such an inverse relationship between heat of adsorption and pore diameter appears to break down for the cases of ferrierite and rho; zeolite rho has a smaller pore diameter than ferrierite but yields a far lower heat of adsorption. One could reasonably argue that the inverse relationship only applies down to a certain pore size below which intermolecular repulsions become dominant and thus reduce the heat of

adsorption. That may well be true, but it is not the explanation for the present values in ferrierite and rho.

In actual fact, the inverse relationship does still apply for the sorption of alkanes in ferrierite and rho, but is necessary to investigate the locations of the sorbed molecules to fully appreciate this. We have recently shown [8] that in the case of zeolite rho, the alkanes are not adsorbed in the 8-ring windows whose diameter is normally used to characterise this material, but in the α -cages, or truncated cuboctahedra, or rho. These α -cages constitute the largest available void volume in zeolite rho. The sorbed alkane molecules feel a pore diameter that is equal to the diameter of an α -cage (approximately 10 Å). The subject of location of the sorbed species is discussed further in the next section.

We have found no experimentally-measured heats of adsorption for the all-silica polymorphs of zeolites rho and ferrierite. As a result of this we are forced to compare our simulated values for the all silica materials with experimentally-measured heats of adsorption on the aluminosilicates. The limited amount of experimental information that we have been able to find is indicated as open symbols in Figure 1. We have previously suggested [8] that the interaction of a $\text{CH}_{2/3}$ group with the Brønsted acid sites generated by the substitution of aluminium into an all-silica framework may be considered as a perturbation from the all-silica case; the rest of the alkane chain does not 'feel' the presence of the acid site and believes that it resides in a siliceous framework. This hypothesis is supported by our findings that the differences between simulated or measured heats of adsorption on all-silica zeolites and measured heats of adsorption on the equivalent aluminosilicate often appear to be independent of the carbon number. In other words, the all-silica heats of adsorption are lower than the aluminosilicate analogue by an approximately constant amount. This is illustrated by the silicalite/ZSM-5 system. In this case, there is experimental data available to compare the simulated heats of adsorption to, and good agreement is found. Furthermore, the simulated heats of adsorption for *n*-butane to *n*-decane in silicalite are approximately 10 kJ/mol lower than experimental measurements of the same alkanes sorbed on ZSM-5 [8].

We have investigated the influence of temperature upon the heats of adsorption and Henry coefficients of the alkanes adsorbed in ferrierite. The values at temperatures of 398 and 498 K are reported in Table II. At both temperatures, straight line graphs are obtained for the heat of adsorption or Henry coefficient as a function of carbon number. The heat of adsorption of the alkanes decreases with increasing temperature at a slow rate; approximately 0.45 kJ/mol/100 K and 1.9 kJ/mol/100 K for butane and

TABLE II Heat of adsorption, Q , and Henry coefficient, K_H values for alkanes in all-silica ferrierite at 398 and 498 K

Temperature [K]	Alkane chain length	Q [kJ/mol]	$\ln K_H$ [ln(mg/g)/atm]
398	C ₄	-50.4	6.91
	C ₅	-63.3	8.94
	C ₆	-77.1	11.51
	C ₇	-90.6	14.13
	C ₈	-104.6	16.82
	C ₉	-117.9	19.34
	C ₁₀	-131.5	21.66
498	C ₄	-49.8	4.08
	C ₅	-62.6	5.38
	C ₆	-75.9	7.11
	C ₇	-89.1	8.85
	C ₈	-102.9	10.65
	C ₉	-116.3	12.39
	C ₁₀	-129.5	14.09

decane, respectively. These rates of decrease are similar to those found for the decrease of the heat of adsorption of alkanes in silicalite with increasing temperature [4, 8]. The natural logarithm of the Henry coefficient, expressed in units of (mg/g)/atm, decreases at a rate of 3.8/100 K for butane and 10.6/100 K for decane.

Location and Conformation of Sorbates

In the previous section, it was mentioned that the simulations of adsorption of alkanes in zeolite rho predict the sorbates to be located with the α -cages that are the building blocks of the structure, rather than within the narrow double-eight ring windows that connect them. This mode of sorption is somewhat surprising, especially for longer chain molecules such as decane, which are forced into increasingly coiled conformations within the cages. As part of the analysis procedure, we locate the centre of the backbone of the sorbed alkanes from the conformational snapshots saved at regular intervals throughout the calculations. Examining the distribution of a large number of backbone locations allows to assess which regions of the pore space are visited. Animation A shows how the double-eight rings in the rho structure are not populated by the centre of the alkane backbone (in this case, decane). Choosing the centre of the alkane chain as a measure of pore accessibility is essentially arbitrary; a plot of the terminal CH₃ groups rather than the midpoints yields an identical picture.

Figure 4 indicates the extent of the conformational changes induced upon sorption, as determined by an analysis of the dihedral angles of the alkane

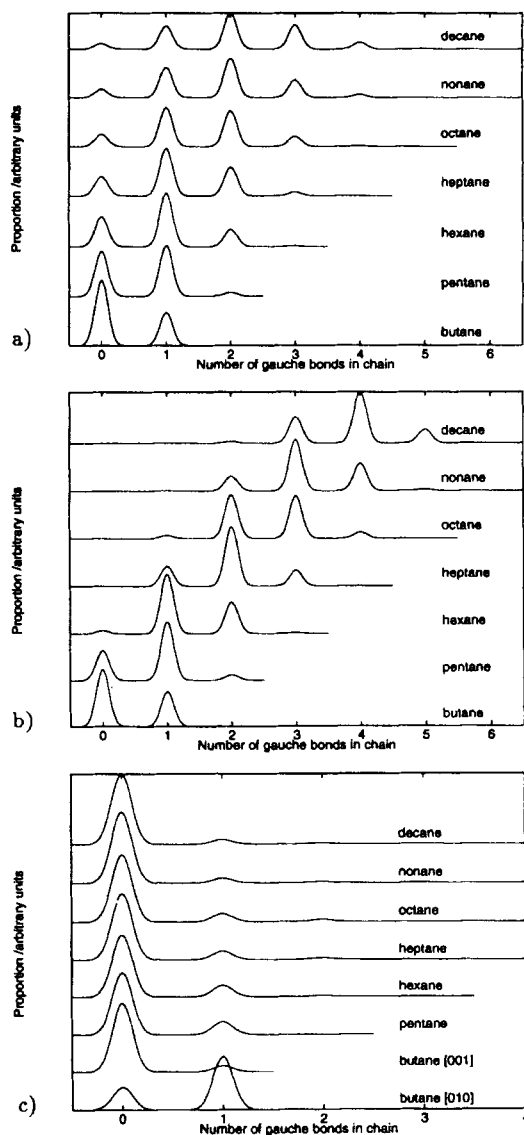
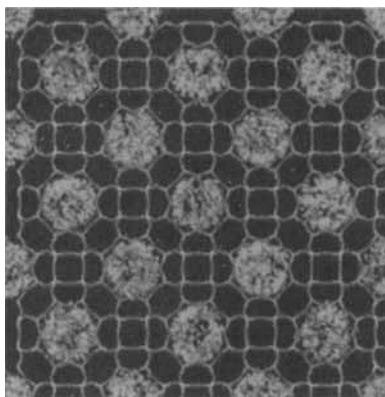


FIGURE 4 Graphs of the distribution of the number of gauche bonds per chain averaged over 10000 chains: (a) Free alkanes : (b) Alkanes sorbed in rho: (c) Alkanes sorbed in ferrierite.

snapshots collected during the simulations. What is plotted in this figure are the relative proportions of the number of gauche bonds in chains of each alkane type. Figure 4a shows data for alkanes in the gas phase, *i.e.* without a zeolite present. In Figure 4b an equivalent set of curves is shown for the



Animation A

FIGURE 5a The location of the centre of the carbon backbones of decane molecules sorbed inside the α -cages of zeolite rho. (Each blue dot represents the centre of one molecule, demonstrating how the double eight-ring windows that connect the cages remain empty. The framework silicon atoms are orange, the oxygens red) (See Color Plate II).

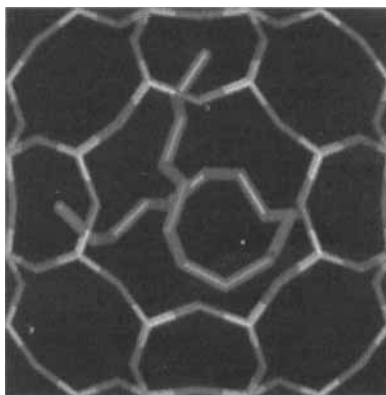
alkanes sorbed within the α -cages of rho. The difference between the two figures is striking, reflecting the severe constraints placed on the alkane conformation by confinement within the pores. Not only does the range of distribution of the number of gauche bonds decrease upon sorption, the modal number of gauche bonds per chain is seen to increase with increasing chain length. Chains in an all-*trans* conformation are not found in significant proportions for alkanes longer than hexane, the length of which (9.7 Å [1]) is comparable to the largest internal diameter of an α -cage (approximately 10.4 Å [1, 8]). Whatever entropic penalties are incurred by coiling longer chain molecules within an α -cage, these must be more than offset by the favourable intermolecular interactions between the alkane and the zeolite wall, as the increasing heat of adsorption as a function of carbon number shows.

We have performed additional calculations to investigate the extent of coiling for very long chain alkane molecules, and to assess the thermodynamic driving force for sorption. Eicosane ($C_{20}H_{42}$) adsorbs in a similar manner to decane; the whole of the carbon backbone is contained within a single cage. This is illustrated in Animation B. (Only in a very small number of high energy cases do the head and tail of the eicosane molecule occupy neighbouring α -cages). The heat of adsorption of eicosane in zeolite rho is estimated to be 140 ± 5 kJ/mol, which is close to the value estimated from the slope of the line on Figure 2 (131 kJ/mol) [10]. We also performed a

short set of illustrative calculations on octatetracontane ($C_{48}H_{98}$). For a chain of this length, we do indeed find that the head and the tail of the alkane chain are in neighbouring (or even next-neighbouring) α -cages.

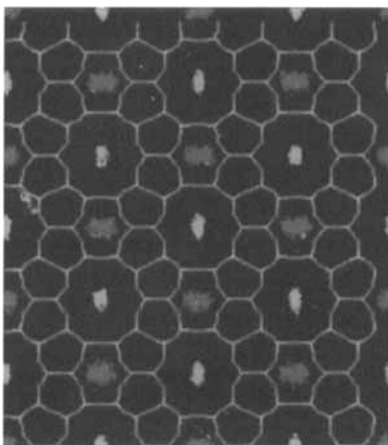
The location of the alkane molecules in ferrierite is somewhat more complex than rho, due to the anisotropic pore structure of ferrierite. In the case of butane, we find that the sorbed species are distributed over both the 10-ring and the 8-ring channels in an approximate ratio of 2:1. This distribution is illustrated in Animation C. The butane molecules in the larger 10-ring channel have their centres distributed evenly along the length of the channel, whereas those in the smaller 8-ring are located close to the channel centre. There is only slight 'pollution' of the picture; *i.e.* only a very small number of butane molecules that have their end-to-end vector parallel to the z -axis or 10-ring channel direction (indicated in Animation C as blue dots) are actually found within the 8-ring channel. These 'pollutant' cases are invariably those of the least-favourable interaction energy due a mis-match between their conformation and the pore that they are confined within.

Increasing the length of the carbon chain by just one atom to adsorb pentane results in a significant change in the alkane distribution. The pentane molecules are found to sorb exclusively in the larger 10-ring channel. Increasing the chain length successively to decane yields an identical picture; all alkane molecules have an end-to-end vector that is parallel to the z -axis and the centre of the alkane backbone lies within the



Animation B

FIGURE 5b The carbon backbone (in green) of eicosane ($C_{20}H_{42}$) sorbed entirely within an α -cage of zeolite rho. (For simplicity, only one α -cage is visible; the framework silicon atoms are in yellow, the oxygens in red) (See Color Plate III).



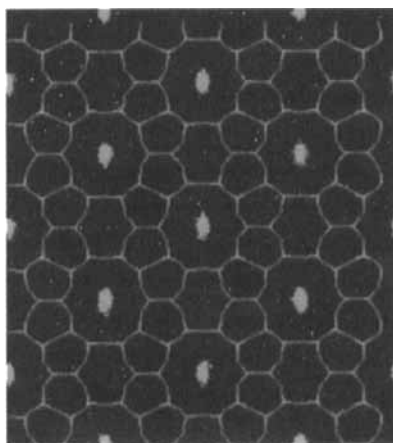
Animation C

FIGURE 5c The location of the centre of the carbon backbones of butane molecules sorbed inside the pore system of ferrierite, viewed down the [001] direction with rotation about [100]. (Purple dots represent molecules with an end-to-end vector parallel to the y-axis and blue dots those parallel to the z-axis. The framework silicons are in orange, the oxygens in red. It can be seen that butane molecules are distributed over the two channels of ferrierite. Those residing in the 10-ring channel are distributed evenly throughout the pore, those in the 8-ring channel are localised near the centre of the channel) (See Color Plate IV).

larger 10-ring channel. This is illustrated in Animation D for *n*-decane (though the animation equally applies to all alkanes of chain length five or more carbons).

According to the results from our sorption calculations, we would predict ferrierite to be a 2-dimensional zeolite to alkanes of chain length 4 (and shorter), while only unidimensional to pentane and longer molecules. A suggestion as to the reason for this decrease in dimensionality is given below, when we discuss the energy of a butane molecule inside each of the two ferrierite channels. Further insights into the sorption and packing of the alkanes within the channels may be obtained by calculating the adsorption isotherms, as has previously been done with the CB-MC method for alkanes in silicalite [11, 12]. We plan to consider such calculations in the future. Another possible direction for future calculations is to consider the migration of a butane molecule in the smaller 8-ring into the larger 10-ring, through a flexible 8-ring window.

We have calculated the average energy of a butane molecule with end-to-end vector parallel to the x-axis (direction of channel intersections), the y-axis



Animation D

FIGURE 5d The location of the centre of the carbon backbones of decane molecules sorbed inside the pore system of ferrierite, viewed down the [001] direction with rotation about [100]. (The colour scheme of dots and framework atoms are as in Animation C. It can be seen that in contrast to butane, only the larger 10-ring channel is populated by decane molecules) (See Color Plate V).

(direction of 8-ring pore) and the z-axis (direction of 10-ring pore). We find the stabilisation is greatest in the 10-ring pore and least in the intersections; the figures are 48.5, 50.3 and 51.1 kJ/mol for butane parallel to the x-, y- and z-axes, respectively. We have previously reported heats of adsorption of alkanes in all-silica zeolites, as a function of pore diameters from 4.8 Å (the 10-ring pore of ferrierite) to 13.4 Å (the diameter of the supercage inside faujasite) [8]. We find a simple inverse relationship between pore diameter and the heat of adsorption within this range. The magnitudes of stabilisation energies of a butane molecule in the 10-ring and one in the intersection of the channels would seem to agree with this inverse relationship; the effective diameter of the intersection is larger than that of the 10-ring and hence the heat of adsorption is lower. However, the 8-ring channel is smaller in diameter than the 10-ring, and should therefore yield a higher heat of adsorption if the inverse relationship still holds. We conclude that this is not the case and at some pore diameter between 4.8 Å (10-ring) and 4.1 Å (8-ring) the repulsive interactions between the zeolite oxygens and the alkane molecules become dominant causing a decrease in the heat of adsorption.

The relative energies of a butane molecule orientated parallel to each of the three axes allow us to speculate on the reason for the reduction in perceived dimensionality of the zeolite moving from butane to pentane. A

butane molecule is able to just fit inside the length of the 8-ring channel, without either of the terminal methyl groups protruding into the intersection, especially if there is one gauche bond in the backbone, which most indeed have (see below). For pentane and longer alkanes, one or even both ends will project into the intersection of the two channels. We have just shown that the inverse relationship between pore size and stabilisation energy means that a $\text{CH}_{2/3}$ unit in the intersection is less stabilised than one in the 8- or 10-ring channels. Thus, the growth of an alkane extending over both the 8-ring pore and the intersection is liable to be less favourable than one completely in the 10-ring pore.

The conformation of the sorbed species within ferrierite is shown in Figure 4c. A distinction is made between the two orientations of the butane molecule. The confinement within the pores produces marked conformational changes when compared to the free, gas-phase alkanes (Fig. 4a). In the case of the butane molecule, it is more twisted in the 8-ring channel and more straight in the 10-ring channel than in the gas-phase. For pentane and higher alkanes we see that the alkane chains tend towards an all-*trans* conformation, forced into this geometry by the confinement within the zeolite pore. The contrasting conformations of alkanes sorbed in zeolites rho and ferrierite are also evident when comparing Figures 4b and c.

The locations and conformations of the alkanes are only slightly influenced by a temperature increase of 200 K. Simulations performed at 498 K show that it is still only the butane molecule that is distributed over the two channels, though approximately 2% of the pentane molecules are found in the 8-ring channel. The pollution of the 8-ring channel by butane molecules with an end-to-end vector parallel to the 10-ring channel does increase, though the amount is still not significant. The distribution of conformations of the sorbed alkanes at 498 K are indistinguishable from those shown in Figure 4c.

CONCLUSIONS

In this paper we have used the CB-MC method to simulate the energetics, location and conformation of *n*-butane to *n*-decane in the pores of all-silica rho and ferrierite. We find that ferrierite stabilises the alkanes far more than rho, and a butane molecule in the 10-ring channel of ferrierite enjoys slightly better stabilisation than one in the smaller 8-ring.

The alkanes in rho are located wholly within the α -cages of the structure, producing highly coiled conformations. This coiling within one cage extends to at least $\text{C}_{20}\text{H}_{42}$. In ferrierite, butane molecules are distributed over the

two channels, but pentane and higher alkanes are located throughout the 10-ring channel only. The conformations of species sorbed in the 10-ring channel are constrained to be almost all in the all-*trans* conformation.

The CB-MC method has been shown to be highly effective in the study of alkane sorption in all-silica zeolites. The extension of this technique to cover more complex sorbates in different frameworks is underway.

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APPENDIX: DETAILS OF THE SIMULATION AND ANALYSIS METHOD

The application of the Configurational-Bias Monte Carlo (CB-MC) method to the simulation of the sorption of chain molecules in micropores has been thoroughly reported elsewhere [2, 11]. Here we present a brief description of the technique as applied to these particular calculations, together with the analysis method used to generate information on the location and conformation of the sorbed alkanes.

The fundamental advantage of the CB-MC method is that it avoids the inherent limitations of 'conventional' Monte Carlo methods as sorbate chain lengths increase. In standard Monte Carlo simulations, the probability of accepting a random insertion of a chain molecule into a void region of the host structure decreases rapidly with increasing chain length. This probability becomes so vanishingly small for moderate- to long-chain molecules – say eight or more carbon atoms – that almost no trial insertions can be accepted.

The CB-MC method avoids this limitation by inserting the first atom of the molecule into the host and 'growing' subsequent atoms until the whole backbone of the molecule is present within the void space of the host. The growth process proceeds by generation of a series of k trial conformations from the most recently grown atom (or inserted, in the case of the first atom). These trial conformations are distributed on the surface of a sphere, with the previous atom at the centre of this sphere. The trial positions are calculated from the "internal" part of the potential – the bond-bending and torsion of the alkanes. (We typically calculate $n + 2$ trial orientations, where n is the carbon number of the alkane under consideration). Note that the distribution of the trial orientations depends on the position of the atom being inserted in the molecule; the first atom to be grown – the second atom of the backbone – generates a random distribution of trial orientations. The third atom of the backbone includes bond-bending terms, and subsequent atoms include torsions as well.

For every trial orientation, the 'external' energy of the system is calculated, *i.e.* the interaction of the growing molecule with the zeolite host and – if more than 4 sorbate atoms are already present – an intramolecular potential value that prevents the growing chain from crossing back on itself. One of these trial positions is selected and the process is repeated until the whole chain has been grown. The acceptance rule that governs the selection of a new alkane conformation in preference to an old conformation is such that the bias introduced by the growing process is removed and a Boltzman

distribution of configurations is generated. The mathematical details of this are documented elsewhere [11].

The simulations were performed in cycles, each of which consists of a randomly selected attempt to either translate, rotate, re-grow part, or re-grow all of the molecule. The latter two choices exploit the CB-MC method. In general at least 10^6 cycles were performed for each alkane in each zeolite, with the fractions of total translation steps : rotation steps : partial re-grows : complete re-grows held fixed at 0.15:0.15:0.6:0.1. The process of completely re-growing a chain inside the zeolite allows us to obtain information with which to calculate the Henry coefficient (defined as the slope of the adsorption isotherm in the limit of zero pressure). We found that 1000 regrows were needed to confidently predict the Henry coefficients and this was the limiting factor for the calculations of sorption in ferrierite, in which up to 5×10^6 total cycles were needed. The Henry coefficients (K_H) were calculated in units of (mg/g)/atm according to the following equation:

$$K_H = \left[\frac{1.207 \times 10^7 M_{\text{alk}} e^{\frac{-\mu_{\text{ex}}}{T}}}{T \rho_{\text{zeo}} e^{\frac{-\mu_{\text{IG}}}{T}}} \right] \quad (1)$$

Here, M_{alk} is the mass of the alkane, T is the temperature (fixed in these simulations at 298 K), ρ_{zeo} is the density of the zeolite (expressed in g/m^3) and μ_{ex} is the excess chemical potential (IG denotes an alkane in the ideal gas state, free from interactions with the zeolite).

The heat of adsorption of the alkanes in the zeolites (Q) at infinite dilution was calculated according to the following formula:

$$Q = \langle U \rangle - \langle U \rangle_{\text{IG}} - k_B T \quad (2)$$

Here, $\langle U \rangle$ is the average energy of the alkane inside the zeolite, $\langle U \rangle_{\text{IG}}$ is the average energy for the same alkane outside the zeolite, *i.e.* in the ideal gas state. The calculation of these values required a separate CB-MC calculation of an alkane sorbed in an infinitely large simulation box. All simulations were performed at 298 K, unless explicitly stated otherwise.

The parameters used for the inter- and intra-molecular potentials are detailed in Table III, along with the functional form of these potentials. The zeolite was assumed to be an all-silica rigid lattice that was not allowed to relax during the simulations. It is believed that this is less of a dangerous assumption in the present 'static' simulations than in, *e.g.* diffusion studies. Only potential parameters from the zeolite oxygen atoms were included in the intermolecular part of the potential – the contributions from the Si

TABLE III Details of potential parameters used in simulations

<i>Internal potential parameters</i>	
Bond stretching $U_{\text{(stretch)}} = \text{constant}$	Fixed bond length = 1.53 Å
Bond bending $U_{\text{(bend)}}(\theta_i) = \frac{1}{2} k_\theta (\theta_i - \theta_e)^2$	$k_\theta = 62500 \text{ K rad}^{-2}$; $\theta_e = 114^\circ$
Bond Torsion $U_{\text{(torsion)}}(\phi_i) = a_1(1 + \cos\phi_i) + a_2(1 + \cos 2\phi_i) + a_3(1 + \cos 3\phi_i)$	$a_1 = 355.03 \text{ K}$; $a_2 = -68.19 \text{ K}$; $a_3 = 791.32 \text{ K}$
<i>External potential parameters</i>	
Non-bonded interactions $U_{\text{LJ}}(r_{ij}) = 4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6]$	$\sigma_{\text{CH}_3} = \sigma_{\text{CH}_2} = 3.93 \text{ Å}$; $\epsilon_{\text{CH}_3} = 114.0 \text{ K}$; $\epsilon_{\text{CH}_2} = 47.0 \text{ K}$; $\sigma_{\text{CH}_3, \text{O}} = \sigma_{\text{CH}_2, \text{O}} = 3.364 \text{ Å}$; $\epsilon_{\text{CH}_3, \text{O}} = \epsilon_{\text{CH}_2, \text{O}} = 84.0 \text{ K}$

atoms are assumed to be implicit in the O atom parameters. The potential at a series of grid points inside the zeolite lattice was determined *a priori*. The potential at an arbitrary point could then be calculation by interpolation during the simulations. It has been noted that using a grid spacing between 0.11 and 0.18 Å yields a reduction in CPU time by a factor of 100 to 300, whilst not compromising the accuracy of the energy (the error is less than 0.4%). In the present calculations, the grid spacings used were 0.127 and 0.152 Å for ferrierite and rho, respectively.

The alkane chains are comprised of united $\text{CH}_{2/3}$ atoms. Simulations were performed at infinite dilution, *i.e.* one alkane molecule only within the zeolite. The zeolite model was composed of an approximately cubic simulation box, to which periodic boundary conditions were applied. For ferrierite, a total of 36 unit cells (2 by 3 by 6) were included in the simulation box, for rho there were 27 (3 by 3 by 3). By coincidence, both simulation boxes contained 2592 oxygen atoms. The crystal structures of the zeolites were taken from the zeolites database of the Biosym Catalysis and Sorption Project Software [15] and any aluminium atoms were replaced by silicon. An all-silica ferrierite has recently been synthesised and characterised [16] but energy minimisation calculations predict it to be very close in energy to that of the previous aluminosilicate structure with all aluminiums replaced by silicon. We have previously discussed the distortion of the all-silica framework of zeolite rho [8] and found this to have a relatively small effect on the predicted heats of adsorption and no effect on the location or conformation of sorbates.

The non-bonded Lennard-Jones interactions were truncated at 13.8 Å, and the usual tail corrections were applied to account for interactions beyond this

cutoff distance. The potential parameters shown in Table III were optimised to reproduce the heats of adsorption of *n*-alkanes in silicalite [2].

At regular intervals throughout the calculations (every 5000 cycles), we took snapshots of the energetics and conformation of the sorbed species for post-calculation analysis. To analyse the location of the various molecules of the different zeolite pore systems, we decomposed the end-to-end vector of each snapshot into components parallel to the three crystallographic axes. The molecular snapshots – or rather the coordinates of the center of the backbone – were then segregated into those which were aligned parallel to the *x*-, *y*- and *z*-axes (by seeing which component of the end-to-end vector was greater than a value, *R*, set equal to 0.707). For zeolite rho, which has cubic symmetry, this division is arbitrary. However, in the case of ferrierite, the division provided valuable information about the proportions of each alkane that are confined within which channel. From this division, we may also calculate the average energy of a molecule parallel to each crystallographic axis, *i.e.* in the case of ferrierite, the energy of a molecule in each type of channel.

Conformations of the sorbed molecules were analysed by evaluating the dihedral angles for each snapshot of each alkane, and then expressing this in terms of the proportion of chains of each alkane with a given conformation, *e.g.* all-*trans*, one gauche bond *etc.*