Structural Investigation of Silicalite-I Loaded with *n*-Hexane by X-ray Diffraction, ²⁹Si MAS NMR, and Molecular Modeling

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The room temperature (298 K) structure of zeolite Silicalite-I loaded with approximately eight *n*-hexane molecules per unit cell was solved from twinned single-crystal X-ray diffraction (XRD) data in the monoclinic space group $P12_1/n1$ with $a = 19.8247(2)$ Å, $b = 20.1292(2)$ Å, $c = 13.4510(2)$ Å, and $\beta = 90.29(8)°$. At this temperature, the guest molecules are dynamically disordered and distributed throughout the entire channel system. The structure determined from a Rietveld refinement of room-temperature powder XRD data, which is not affected by the twinning, confirmed this. A twinned crystal refinement was also carried out for data collected at 180 K ($P12_1/n1$, $a = 19.9310(2)$ Å, $b = 20.1730(3)$ Å, $c = 13.4191(3)$ Å, $\beta = 90.20(5)°$). At 180 K, the sorption sites of the *n*-hexane molecules are well-defined within the channel system, being located only in the straight and sinusoidal channels, leaving the intersections unoccupied. This ordering is commensurate with the framework structure of Silicalite-I. ²⁹Si HPDEC MAS NMR shows that the loading of *n*-hexane induces a phase transition to an orthorhombic space group (most likely *Pnma*) only above 340 K. Force field simulations confirm that the absorption of *n*-hexane molecules occurs only inside the straight and sinusoidal channels and leads to an energetically minimized host−guest structure. By optimizing the van der Waals interactions between the *n*-hexane molecules and the silica host framework, the nonbonding energy is minimized, leading to a general minimization of the total potential energy, and the energetically most favorable structure is obtained.

Introduction

Zeolites are open, crystalline inorganic materials with well-defined pore geometries. To date, crystallographic analyses have mainly focused on the determination of new framework structures with or without their structure directing agents. Some attention has been also paid to the periodic ordering of sorbate molecules inside the zeolite pores.[1] As the pore structures of most zeolites are of molecular dimensions, the interactions of adsorbed alkane molecules should reflect the periodicity of the zeolite channels. Recently, theoretical studies of the behavior of alkanes in Silicalite-I suggested that the molecules freeze in a configuration which is commensurate with the pore structure.[2] In adsorption experiments, short and long chain alkanes exhibit different isotherms which might reflect distinct sorption mechanisms for molecules of various sizes.[3]

In this paper, we present the first results of (twinned) single-crystal X-ray diffraction and NMR analyses of *n*-hexane loaded in zeolite Silicalite-I (structure type MFI, $Si_{96}O_{192}$) combined with computational molecular modeling studies. Whereas the X-ray analysis gives insight into the periodic structure of the zeolite, including the *n*-hexane molecules, NMR probes the short range ordering of the nucleus under investigation. In the computational experiments, we have an instrument both to analyze the system locally and also to probe the periodic order based upon a theoretical model of the interactions. The combination of the three techniques should therefore provide a detailed picture of the arrangement of the sorbate molecules within the zeolite channels.

The framework of Silicalite-I has the MFI topology with a 2-dimensional (2D) connected channel system. The channels are either straight or sinusoidal (Figure 1) and have accessible pore dimensions between 5.5 and 5.8 Å. The crossing of the straight and sinusoidal channels is referred to as the intersection.

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(1) van Koningsveld, H. *J. Mol. Catal. A: Chem.* **1998**, *134*, 89.

(2) (a) Smit, B.; Maesen, T. L. M. *Nature (London)* **1995**, *374*, 42. (b) Vlught, T. J. H.; Krishna, R.; Smit, B. *J. Phys. Chem. B.* **1999**, *103*, 1102. (c) Krishna, A.; Paschek, D. *Phys. Chem. Chem. Phys.* **2001**, *3*, 453. (d) Schuring, D.; Korabinka, A. O.; de Jong, A, M.; Smit, B.; van Santen, R. A. *J. Phys. Chem. B* **2001**, *105*, 7690.
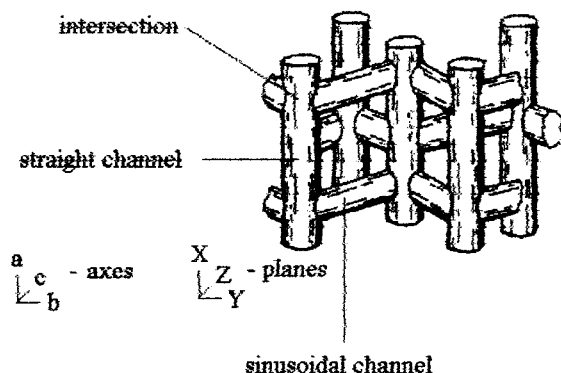(3) Yang, Y.; Rees, L. V. C. *Microporous Mater.* **1997**, *12*, 223.

Figure 1. 2D connected channel system of Silicalite-I showing the sinusoidal and straight channels. A channel intersection is also indicated.

Both the as-synthesized (template containing) and the high-temperature phase of calcined Silicalite-I are orthorhombic with *Pnma* symmetry.[4] During the process of cooling to ambient temperature, the calcined crystals undergo a ferroelastic phase transition, becoming twinned monoclinic (space group $P12_1/n1$) crystals with a domain structure.[5] Normally, both domains occur with 50% probability and are related by the twin matrix [−100, 010, 001] which corresponds to a 180° rotation about the *c* axis. It is important to note that this form of twinning does not disrupt the channel system, nor does it seem to have a large influence on the sorption of molecules since the 2D channel system remains intact with slightly elliptical channels.

Experimental Section

Microcrystalline (powder) Silicalite-I samples were synthezised using tetramethoxysilane (TMOS, Fluka, 99%) and aqueous tetrapropylammonium hydroxide (TPAOH, Aldrich, 1 molar) in the molar ratio of TMOS:TPAOH = 1.7:1.0. The mixture was heated in a Teflon-lined autoclave at 453 K for 10 days. The sample was isolated and heated at a rate of 2 K/min to 813 K and calcined for 96 h. Highly crystalline, purely siliceous Silicalite-I powder was obtained with particle sizes in the range of 5−10 μm. Large (200 × 120 × 100 μm) single crystals of Silicalite-I were synthesized from aqueous solution under hydrothermal conditions in Teflon-lined autoclaves at 453 K for 6 days according to the method of Lermer and Unger.[6] The molar composition was SiO$_2$:NaOH:TPABr:H$_2$O = 12:40:40:2000. The reactants used were Aerosil 200 (Degussa), tetrapropylammonium bromide (TPABr, Fluka, 98%), sodium hydroxide (NaOH, Baker), and deionized water. The crystals were isolated, heated to 813 K at a heating rate of 1 K/min, and calcined for 48 h. Upon removal of the organic template by calcination, single, twinned monoclinic crystals with a domain structure were obtained.

Silicalite-I was loaded with *n*-hexane (Baker, 98%), by placing five crystals in 200 mg of microcrystalline Silicalite-I powder. The sample was heated for 5 h to 500 K in order to evaporate residual sorbates. The temperature was than set to 353 K, and 45 μL of *n*-hexane was added. This corresponds formally to 10 molecules per u.c. (unit cell) of Silicalite-I. The excess of sorbate was used in order to ensured that the maximum loading (8 molecules/u.c.)[7] was achieved. The Silicalite-I/*n*-hexane mixture was kept in a sealed glass tube at

353 K for 6 h. Thermogravimetric measurements were carried out heating the sample up to 650 K in a Linseis L81/075 thermobalance to verify the loading.

To investigate possible symmetry changes in the loaded form of Silicalite-I,[8] high-power proton-decoupled (HPDEC) ^{29}Si MAS NMR measurements were carried out at room temperature on a Bruker ASX 400 spectrometer using a 7 mm Bruker MAS probe (spinning frequency 3.5 kHz, recycle delay 4 s, 90° pulse length 10 μs).

The single-crystal X-ray experiments were carried out on a Rigaku diffractometer (ACF7 with ADSC CCD detector) using graphite-monochromated Mo Kα radiation. Immediately after loading and sealing the single crystals in 0.1 mm capillaries, they were cooled in liquid nitrogen and mounted on the diffractometer goniometer. For comparison, measurements were also carried out using a single-crystal wedged above a small amount of liquid *n*-hexane in a sealed capillary. This ensured maximum loading was maintained throughout the diffraction experiment. Within the WinGX package,[9] the SHELX-97-2 program[10] was used for structure analysis. The refinement was carried out with full-matrix least-squares methods on F^2. No merging of reflections was applied in the refinement of the intensity data for the twinned crystals.

The powder diffraction experiment was carried out in Debye Scherrer transmission geometry on a D5000 diffractometer from Siemens using Ge-[111] monochromated Cu Kα_1 radiation and a 0.3 mm sealed capillary. For the Rietveld refinement, the program package XRS-82[11] was used.

Molecular modeling experiments were carried out using the program Insight-II from Molecular Simulations.[12] A combination of Monte Carlo simulations and energy minimization, both on the basis of empirical covalent valence force fields, was used.[13]

Results and Discussion

^{29}Si MAS NMR. The crystallinity and symmetry of the Silicalite-I powder was checked by ^{29}Si HPDEC MAS NMR. Depending on the degree of condensation, the ^{29}Si NMR signals can be grouped in different frequency ranges. Whereas the ideal tetrahedral framework of an all-silica zeolite contains only [SiO$_4$]-tetrahedra linked to four other tetrahedral units (Q^4-silicons, Si(4Si)) and gives rise to NMR signals in the range of −106 to −122 ppm (relative to TMS), defect structures have partially condensed frameworks with, e.g., [SiO$_4$]-tetrahedra linked to only three other tetrahedra and one hydroxyl group (Q^3-silicons, Si(3Si,1OH)). The NMR signals of these units show resonance frequencies in the range of −94 to −104 ppm. The as-synthesized sample showed two groups of rather broad ^{29}Si signals, one for Q^4-silicons and one for Q^3-silicons indicating that the condensation process was incomplete. After calcination, the spectrum showed only Q^4 ^{29}Si-signals. The resolution of the spectrum was extremely good, and 17 of the 24 peaks corresponding to the 24 symmetrically inequivalent T-sites in the monoclinic asymmetric unit[14] (Figure 2a) are resolved.

(4) van Koningsveld, H. *Acta Crystallogr.* **1990**, *B46*, 731.

(5) van Koningsveld, H.; Jansen, J. C.; Van Bekkum, H. *Zeolites* **1990**, *10*, 235.

(6) Lermer, H.; Draeger, M.; Steffen, J.; Unger, K. K. *Zeolites* **1985**, *5*, 131.

(7) van Well, W. J. M.; Wolthuizen, J. P.; Smit, B.; van Hooff, J. H. C.; van Santen, R. A. *Angew. Chem.* **1995**, *107*, 2765.
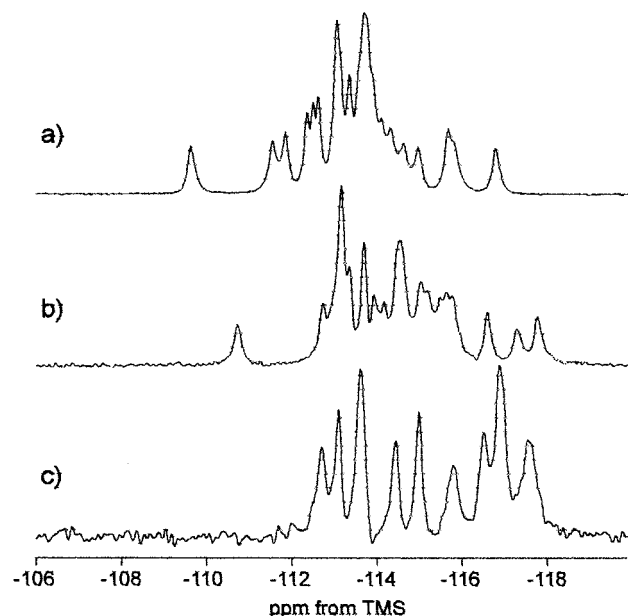
(8) Fyfe, C. A.; Strobl, H.; Gies, H.; Kokotailo, G. T. *Can. J. Chem.* **1988**, *66*, 1942.

(9) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(10) Sheldrick, G. M. SHELX-97(2): A Program for the Refinement of Crystal Structures. University of Göttingen, Göttingen, Germany, 1997. http://shelx.uni-ac.gwdg.de/SHELX/.

(11) Baerlocher, C. *Zeolites* **1986**, *6*, 325.

(12) MSI, Discover 2.9.7/95.0/3.00 - Force field Simulations. *User Guide, Part 1–3*; Molecular Simulations: San Diego, CA, 1995.

(13) MSI, Catalysis 3.0.0 - Materials Modeling Software. *User Guide*; Molecular Simulations: San Diego, CA, 1995.

(14) Fyfe, C. A.; Grondey, H.; Feng, Y.; Kokotailo, G. T. *J. Am. Chem. Soc.* **1990**, *112*, 8812.

Figure 2. ^{29}Si HPDEC MAS NMR spectra: (a) calcined Silicalite-I at 293 K showing 17 of the 24 possible Q^4 signals between -109 and -118 ppm corresponding to the 24 monoclinic T-sites in the asymmetric unit; (b) Silicalite-I loaded with 8 molecules of *n*-hexane per unit cell at room temperature showing 16 of 24 possible Q^4 signals between -110 and -119 ppm corresponding to the 24 monoclinic T-sites in the asymmetric unit; (c) Silicalite-I loaded with 8 molecules *n*-hexane per unit cell at 340 K showing 10 of 12 resonances between -112 and -119 ppm corresponding to the 12 orthorhombic T-sites in the (*Pnma* symmetry) asymmetric unit. No peaks were observed between -95 and -102 ppm indicating the absence of Q^3 defects, and the recycle delay was set appropriately to ensure the spectra are quantitatively reliable.

After loading the Silicalite-I sample with *n*-hexane, the symmetry of the unit cell was checked. The ^{29}Si HPDEC MAS NMR spectrum showed 16 resolved resonances (with a total intensity corresponding to 24 silicon sites) at approximately the chemical shifts expected for the monoclinic phase of the zeolite framework (Figure 2b). This confirmed that no phase change to orthorhombic *Pnma* symmetry (12 inequivalent silicon T-sites) had occurred. This differs from the sorbate-induced phase changes to *Pnma* symmetry observed with various para-substituted aromatic species.[8,15–21] However, when the ^{29}Si spectra of the unloaded and loaded forms are compared, the low field peaks shift significantly to higher field on loading, suggesting that the monoclinic angle of the unit cell has decreased and is now very close to 90°. Further details are presented following the analysis of the diffraction data.

A phase transition of the fully hexane-loaded sample is observed when it is heated to 340 K and the number

(15) Fyfe, C. A.; Strobl, H.; Kokotailo, G. T.; Kennedy, G. J.; Barlow, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 3373.
(16) Klein, H.; Fuess, H.; Ernst, S.; Weitkamp, J. *Microporous Mater.* **1994**, *3*, 291.
(17) Mentzen, B. F. *Zeolites* **1993**, *13*, 485.
(18) Mentzen, B. F.; Lefebvre, F. *J. Chim. Phys. Phys.-Chim. Biol.* **1998**, *95*, 1052.
(19) van Koningsveld, H.; Tuinstra, F.; Van Bekkum, H.; Jansen, J. C. *Acta Crystallogr.* **1989**, *B45*, 423.
(20) van Koningsveld, H.; Jansen, J. C. *Microporous Mater.* **1996**, *6*, 159.
(21) van Koningsveld, H.; Koegler, J. H. *Microporous Mater.* **1997**, *9*, 71.

Table 1. Parameters for the Room Temperature High-Loaded Silicalite-I/*n*-Hexane Single Crystal X-ray Structure Refinement

chem formula	$Si_{24}O_{48} \cdot 1.43 C_6H_{14}$
unit cell dimens	
a, Å	19.8247(2)
b, Å	20.1292(2)
c, Å	13.4510(2)
α, deg	90.0
β, deg	90.29(8)
γ, deg	90.0
cell vol, Å^3	5364.9(5)
Z	4
space group sym	$P12_1/n1$
data collcn temp, K	293
no. of reflcns with $I > 6\sigma(I)$	28 002
index ranges	$-23 \le h \le 23$
	$-23 \le k \le 23$
	$15 \le l \le 12$
$2\theta_{max}$, deg	50
no. of free params in refinement	762
largest diff max. and min. in E-map, e Å^{-3}	1.56 and -1.21
R_{exp}	0.080(9)
R_1	0.111(7)
wR_2	0.339(6)
GooF (goodness of fit) on F^2	2.66(8)

of resolved ^{29}Si NMR signals is reduced to 10 (Figure 2c). This can be simulated with 12 peaks corresponding to the 12 T-sites of equal occupancy in the silica framework expected for orthorhombic *Pnma* symmetry. Compared to the empty (calcined) sample, the transition temperature is reduced by about 30 K.[5] As indicated by the systematic shift of the low field NMR signals, the internal pressure built up by loading the sorbate molecule stresses the silica framework, but not enough to induce completely the phase transition at room temperature. Only the combined action of sorption and temperature leads to the phase transition, but at a temperature 30 K lower than that for the empty framework. A similar lowering of the phase transition temperatures in highly siliceous MFI zeolite samples loaded with *p*-xylene and *p*-dichlorobenzene has been reported previously.[15]

Single Crystal and Powder Diffraction Structure Refinements. A summary of the data collection and refinements for the high-loaded single crystal at room temperature is presented in Table 1. For the structure refinement of the host framework, the symmetry setting and fractional coordinates for silicon and oxygen atoms as published by van Koningsveld in ref 22 were used. The refinement of the twinned crystal using the TWIN command in SHELX-97[10] with anisotropic displacement parameters converged, yielding the expected distances and angles for the silica framework. Electron density maps, ρ(obs), were calculated using the phase information determined from the partial structure, to locate the sorbate molecules. Since the structure is centrosymmetric, any residual errors in the phases obtained from the partial structure are negligible, yielding a precise electron density distribution due to the sorbate molecule. This gives a space-averaged image of the location and orientation of the sorbate molecule inside the zeolite channel system. In an effort to clarify the location of the sorbate molecules, the contrast in the

(22) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*, 3rd ed.; International Zeolite Association, Butterworth-Heinemann: Boston, MA, 1992.
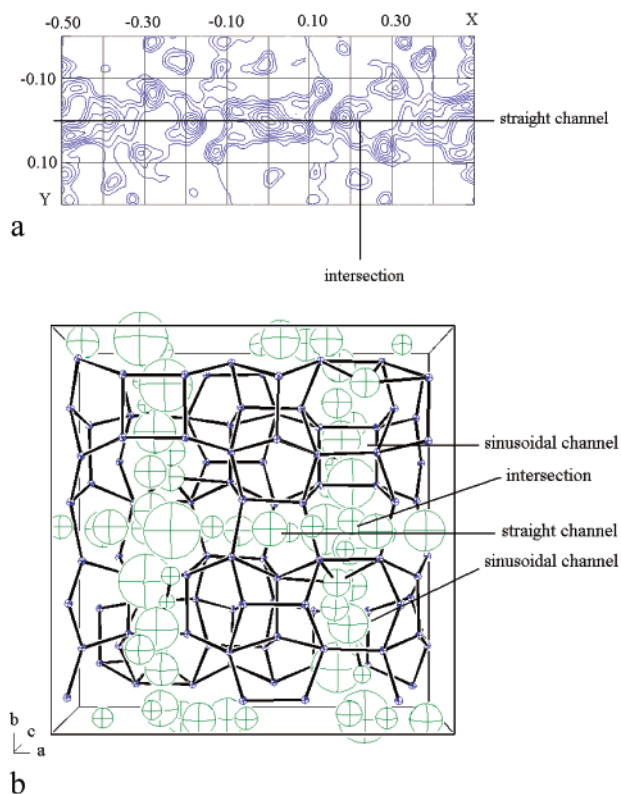
a

b

Figure 3. (a) View parallel to the x−y plane at $z = 0.5$ showing straight channel ($0 \leq x \leq 0.5$, $-0.1 \leq y \leq 0.1$, 0.15 eV contours). The electron density difference in this region appears to be disordered. (b) Carbon atoms inside the channel system of Silicalite-I at room temperature as a numerical fit to the measured electron density. The spheres represent the temperature factors, which are sometimes very large due to the high degree of disorder.

graphical representation was increased by calculating electron density difference maps (E-maps), ρ(obs) $-$ ρ-(calc(Si,O)). Since the X-ray intensity data are subject to the monoclinic space group symmetry, the Fourier calculation yields electron densities with the intrinsic space group symmetry. The difference electron density maps show no commensurate, periodic ordering of the sorbate molecule inside either the straight or sinusoidal channels. In Figure 3a, a section crossing half a unit cell is shown parallel to the *x,y*-plane at $z = 0.5$. The *E*-map shows delocalized electron density along the channels and also at the intersections. This representation of the scattering contribution of the disordered sorbate molecule in an electron density map is the most fundamental experimental result which can be obtained.

To simulate the scattering contribution of the sorbate in the structure refinement and to obtain the best possible fit of a model structure to the experimental data set, carbon atoms as scatterers were located at positions corresponding to the experimental electron density maxima, and their site occupancy factors (SOF) and isotropic displacement parameters (U_{iso}) refined. This yields a computational representation of the disordered sorbate molecule in the structure for the purpose of the structure refinement only. As noted above, the most physically relevant picture of the distribution of the sorbate molecule distribution in the zeolite is that given by the electron density map.

Figure 3 presents a graphical representation of the final results for the single-crystal structure refinement

Table 2. Parameters for the Rietveld Refinement of the High-Loaded Silicalite-I/*n*-Hexane Powder X-ray Diffraction Data

acceleration voltage, kV	50
heating power, mA	30
range (2θ), deg	7−77
mode	step scan
time per step, s	1000
step width (2θ) deg	0.0078
no. of used reflcns	2902
no. of max. overlapping reflcns	132
no. of struct params	435
data collcn temp, K	293
no. of geom restraints	288
no. of profile params	10
unit cell dimens	
a, Å	19.9111(2)
b, Å	20.1346(1)
c, Å	13.4081(4)
α, deg	90.0
β, deg	90.5(1)
γ, deg	90.0
cell vol, Å^3	5375.13
chem formula	$Si_{24}O_{48} \cdot 1.92 C_6H_{14}$
Z	4
space group	$P12_1/n1$
R_F	0.066
R_I	0.091
R_{wp}	0.1066
R_{exp}	0.077
χ^2	1.89

of the Silicalite-I/*n*-hexane complex at room temperature which gives the *R* factors reported in Table 1. A complete listing of the fractional atomic coordinates and thermal parameters is given in the Supporting Information.

For comparison with the single crystal data, the Rietveld analysis of a powder X-ray data set of Silicalite-I fully loaded with *n*-hexane recorded at room temperature was carried out to test the results of the refinement of an isolated single crystal against that of the powder technique, which probes the whole (bulk) sample (Table 2). As for the (twinned) single-crystal analysis, the Rietveld refinement of the powder data set was based on the data for calcined MFI in ref 22. The numerical fit of the powder data set leads to a result which is in general agreement with the single-crystal data set; at room temperature, the *n*-hexane molecules are disordered and occupy both channels and the intersections. This is particulary satisfying since the number of structural parameters is very high and at the limit of the technique, particularly for laboratory X-ray powder diffraction equipment. Final fractional coordinates and site occupancy factors found from the Rietveld refinement are given in the Supporting Information. The high temperature and site occupancy factors of the structure represent the best numerical fit to the experiment and indicate a high level of disorder. Figure 4 shows a graphical representation of the final host−guest structure from this refinement. The general features of the stucture are identical to those from the single-crystal refinement at room temperature shown in Figure 3b.

The (twinned) single-crystal refinement for the *n*-hexane-loaded MFI-crystal XRD data collected at 180 K was treated as exactly as described above and the details are summarized in Table 3. In contrast to the disordered arrangement of the *n*-hexane sorbate molecules at room temperature, clear periodic ordering
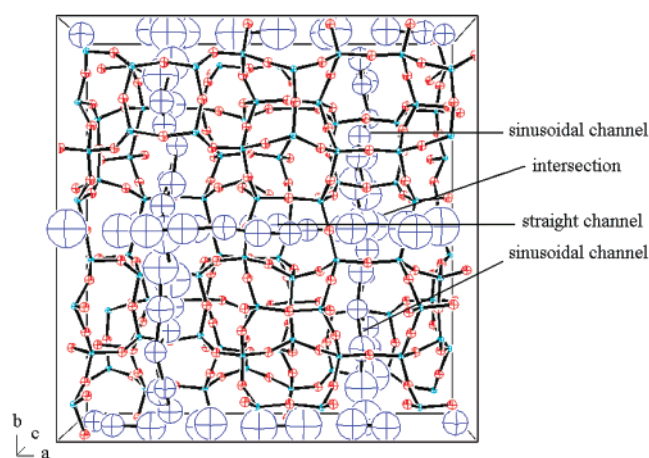
Figure 4. Graphical representation of the final result of the Rietveld refinement of the high-loaded Silicalite-I/*n*-hexane powder X-ray data at room temperature. The spheres represent the temperature factors, which are sometimes very large due to the high degree of disordering.

Table 3. Parameters for the Single Crystal Refinement of High-Loaded Silicalite-I/*n*-Hexane at 180 K

chem formula	$Si_{24}O_{48} \cdot 1.26C_6H_{14}$
unit cell dimens	
a, Å	19.9310(2)
b, Å	20.1730(3)
c, Å	13.4191(3)
α, deg	90.0
, deg	90.20(5)
γ, deg	90.0
cell vol, Å^3	5395.3(2)
Z	4
space group sym	$P12_1/n_1$
no. of reflcns with $I > 6\sigma(I)$	20 989
index ranges	$-23 \leq h \leq 23$
	$-23 \leq k \leq 23$
	$15 \leq l \leq 12$
$2\theta_{max}$, deg	50
no of free params in refinement	837
largest diff max. and min. in E-map, e Å^{-3}	1.63 and -1.07
R_{exp}	0.073(5)
R_f	0.073(9)
R_{wp}	0.222(1)
GooF (goodness of fit) on F^2	1.65(8)

along the channels is observed at 180 K. The electron density difference maps clearly indicate that the sorbate molecules exhibit long range order, residing only inside the straight and sinusoidal channels. No residual electron density maxima are observed at the channel intersections, indicating that they are not occupied by *n*-hexane. Figure 5 shows the electron density difference maps (at $z = 0.5$ and $x = -0.274$) through the center of both channel types. It is obvious from these electron density maps, particularly Figure 5b, that there is spacial ordering of the sorbate molecules inside the channels but not within the channel intersections. However, the sorbate molecules still exhibit static and/or dynamic disorder on a local scale. The electron density maxima obtained from the Fourier calculations do not represent single positions of specific atoms of the sorbate molecule but rather the average scattering centers obtained by considering the intrinsic symmetry in the intensity data set, the static and/or dynamic disorder of the sorbate molecules inside the channels, and their conformational degrees of freedom. *R* factors
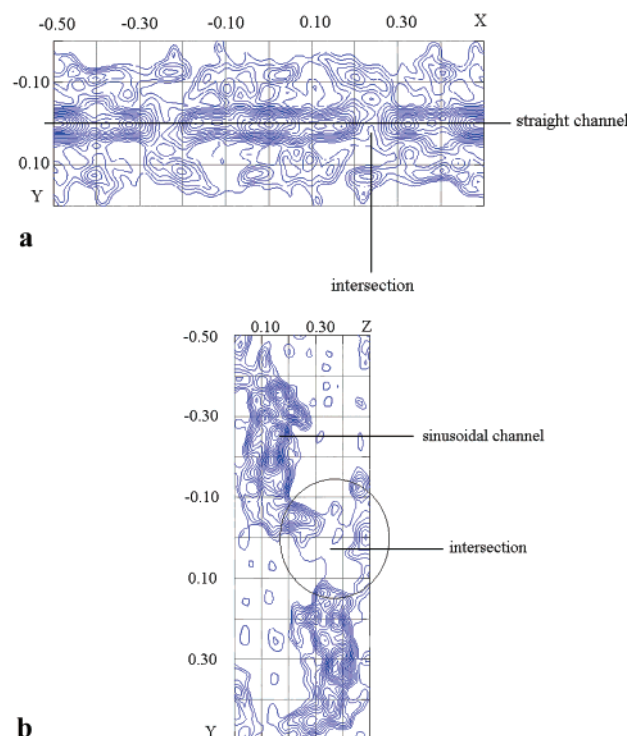

Figure 5. Fourier difference maps of the Silicalite-I/*n*-hexane complex showing that the electron density appears to be strongly ordered and the intersections are unoccupied. (a) View of the straight channel, parallel to the x−y plane at $z = 0.5$ ($0 \leq x \leq 0.5$, $-0.1 \leq y \leq 0.1$). (b) View of the sinusoidal channel, parallel to the y−z plane at $x = -0.274$ ($-0.5 \leq y \leq 0$, $0 \leq z \leq 0.25$). The contour levels are at 0.15 eV spacing.

for the Silicalite-I/*n*-hexane single-crystal refinement at 180 K are reported in Table 3, and the fractional atomic coordinates, site occupancies, and thermal parameters is available in the Supporting Information.

The numerical fit of the scattering contributions of the sorbate molecule was again optimized by positioning carbon atoms at suitable sites for the sorbate molecules, and allowing their site occupancies and displacement paramenters to refine. This yields a reasonable structure model with the *n*-hexane molecules being ordered exclusively inside the straight or sinusoidal channels with unoccupied voids at the intersections. The ordering of the sorbate molecules is therefore commensurate with the host framework structure (Figure 5). To visualize the best numerical fit of the refinement, a molecular representation (based, as previously, on the van der Waals radius of carbon) of the sorbate molecule electron density at the sites obtained from the refinement is produced (Figure 6).

Computer Modeling Studies. Modeling of the zeolite-sorbate host−guest structures was performed in the MSI Insight-II environment.[13] In the first step, a large number ($n = 10000$) of *n*-hexane conformations each with a different geometry were calculated. A random selection of of these conformers was then added to random positions in the Silicalite-I unit cell, in each case up to the desired maximum number of molecules per unit cell. The total potential energy of the system was then calculated using a covalent valence force field (CVFF) with terms for bond lengths, bond angles, torsion angles and [6-12] Lennard-Jones potentials for the nonbonding interactions.[13]
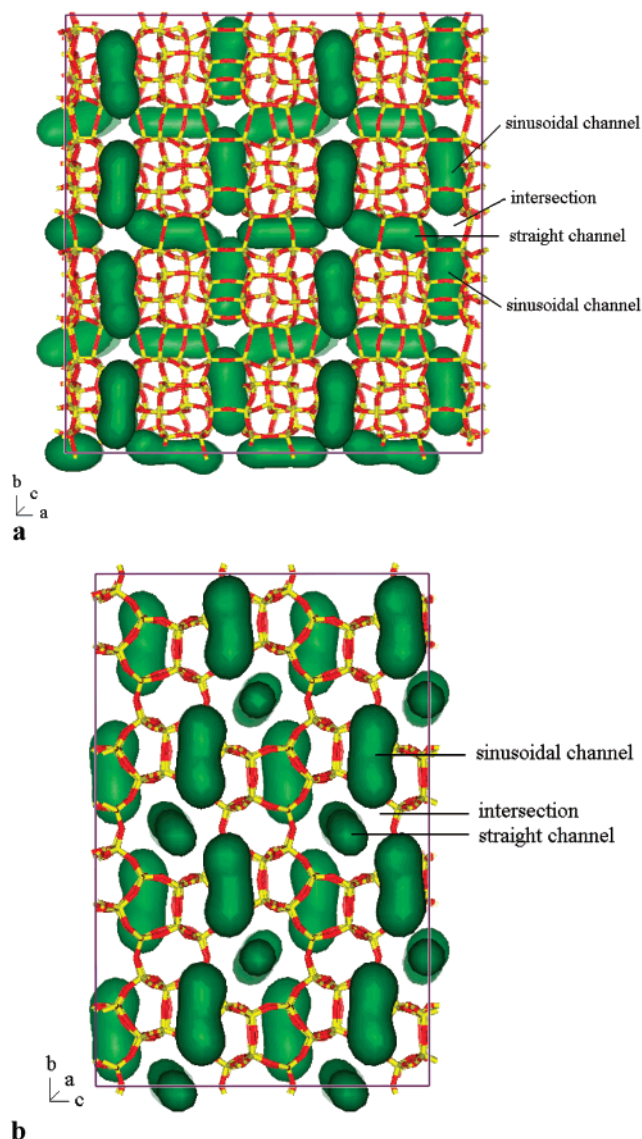
Figure 6. Graphical representation showing the best numerical fit to the electron density showing the location of the guest molecules inside the straight and sinusoidal channels: (a) view along the *c* axis; (b) view along *a* axis. The *n*-hexane molecules appear to be strongly ordered and the intersections are unoccupied. van der Waals radii have been used for the carbon atoms.

Default parameters from the CVFF-MSI force field were used as provided by the program package.[12,13] Different host−guest structures were calculated until all the previously obtained conformers had been used, resulting in only 38 host−guest structures with no overlap between *n*-hexane molecules with the framework or with other *n*-hexane molecules. Each *n*-hexane molecule in these structures had a slightly different conformation, because they were all chosen randomly from the 10 000 previously calculated conformeres. In the next step, a simulated annealing process was performed on only those 38 host−guest structures with no overlaps. To allow the guest molecules to change position and conformation inside the channels, the simulated annealing calculation was carried out at different temperatures (1000, 700, and 500 K and room temperature), so that the total potential energy in the system was slowly reduced. In the final step, an energy
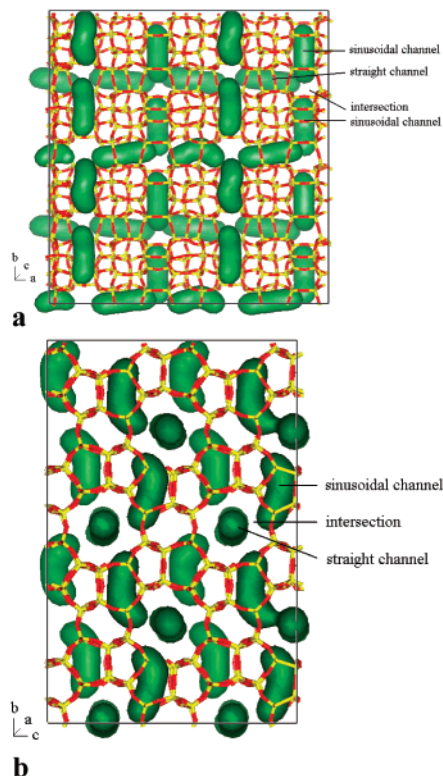

Figure 7. Illustration of the lowest total potential energy host−guest structure found in the computer simulations showing the location of the guest molecules inside the straight and sinusoidal channels: (a) view along *c* axis; (b) view along *a* axis. The molecules are strongly ordered and located only inside the channels leaving the intersections free. Note that a unit cell contains only eight different *n*-hexane molecules, which are replicated by symmetry. van der Waals radii have been used for the carbons.

minimization procedure was used to calculate the final total potential energy of the system. During all calculations, a rigid framework with monoclinic symmetry was used. The discussion of the results is based on these final energies and the positions of the guest molecules on different sorption sites inside the channel system.

To compare the results with those from the single-crystal structure analyses, the arrangement of eight molecules of *n*-hexane per unit cell was simulated first. In the host−guest structures having the lowest total energy, the molecules were strongly ordered. They were exclusively located inside the channels, leaving the intersections unoccupied (Figure 7). These calculations indicate that this host−guest configuration is the energetically most stable and therefore favored thermodynamically. This result is in excellent agreement with the single-crystal analysis and the previous calculations of Smit and Maesen.[2]

A comparison between the host−guest structures with the lowest (E_{min}) and second lowest (E_{min2}) values of total potential energy shows that the molecules in E_{min2} are disordered. The molecules absorb in a nonregistered fashion inside the channel system and also at the intersections. The differences in total potential energy between E_{min2} and E_{min} ($\Delta E_{total} = E_{min2} - E_{min}$ [kcal/mol]) equals 9 kcal/mol, indicating a stable energy minimum for the ordered arrangement for the guest molecules inside the host, at least at low temperatures.
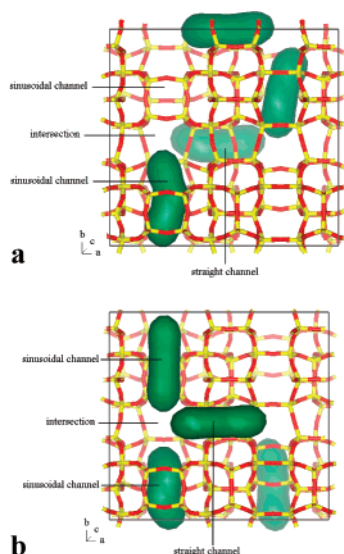
Figure 8. Two types of host–guest structures found from simulation of Silicalite-I loaded with 4 *n*-hexane molecules per u.c. (a) Structure type 1: two molecules are located in each of the straight and the sinusoidal channels. (b) Structure type 2: one molecule is located in the straight and three are in sinusoidal channels. In both cases the molecules are strongly ordered, leaving the intersections unoccupied.

By analyzing the different energies which contribute to the total potential energy of the structures, it was found that the nonbonding van der Waals interactions are the most important in determining the locations of the molecules. An energy difference ($\Delta E_{nonbond}$) of 7 kcal/mol between E_{min2} and E_{min} was obtained, and the minimization of the nonbonding energy leads to a general minimization of the total potential energy and so to a stable total potential energy minimum. The minimization of the nonbonding energy is achieved by maximizing the van der Waals interactions between the guest molecules and the host framework. It is clear that this optimization of the van der Waals interactions takes place inside the channel system and not in the intersections, where the distances between the guest molecules and the host are much larger. This shows that the energy minimum is only reached if the molecules adsorb in a strongly ordered fashion within the channels, leaving the intersections free and thereby maximizing the van der Waals interactions.

In addition, the molecular distribution for a loading of four molecules of *n*-hexane per unit cell was also simulated. Two major types of host–guest structures were found, both with molecules strongly ordered and located only inside the channels, leaving the intersections free. Because only four molecules were used, there are two different ways the molecules can be arranged inside the channels of a single unit cell: (i) two molecules inside the straight channel and two molecules inside the sinusoidal channel (Figure 8a) or (ii) three molecules inside the sinusoidal channel and only one molecule in the straight channel (Figure 8b). The difference between the total energies ΔE_{total} for these two configurations is very small, only 1 kcal/mol, indicating that neither arrangement is preferred.

In contrast, the difference in the total potential energy between these two structure types and the next energetically higher disordered host–guest structure with occupied intersections is 8 kcal/mol. The energy difference for the nonbonding energy also shows a large difference of 7 kcal/mol. As in the case of eight molecules per unit cell, the ordered host–guest structure types appear to be energetically more stabilized and show significant minima in the total energy. No simulations yielded structures having all molecules located in only the straight or in the sinusoidal channels, indicating that neither structure leads to energetically more preferred host–guest structures.

Conclusions

We have demonstrated that the ordering of *n*-hexane molecules in Silicalite-I is strongly temperature dependent. At room temperature, the sorbate molecules are dynamically disordered and distributed throughout the whole channel system. This result was obtained from both (twinned) single crystal and powder diffraction experiments with good and detailed agreement between the two methods. At 180 K the *n*-hexane molecules are well-defined and ordered within the channel system, being located only in the straight and sinusoidal channels but leaving the intersections unoccupied.

The computer simulations show that by maximizing the van der Waals interactions between the *n*-hexane molecules and the silica host framework, the nonbonding energy is minimized, which leads to the energetically most favorable structure. For *n*-hexane, the interactions between the guest molecules and the host silica framework are not sufficiently strong to induce a phase transition at room temperature. In the case of four molecules per unit cell, two energetically comparable host–guest structures were found. In both of these, the *n*-hexane molecules are strongly ordered in terms of location and occupy only the straight and sinusoidal channels again leaving the intersections free.

Supporting Information Available: Tables listing atomic positional (fractional) coordinates, site occupancy factors, and thermal parmameters for the Si, O, and C atoms for the room-temperature single crystal and powder (Rietveld) refinements as well as the 180 K single-crystal refinement and a table with the CVF force field parameters used for the energy calculations (PDF). This material is available free of charge via the Internet at http://pubs/acs.org.