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Molecular-dynamics analysis of the diffusion of molecular hydrogen in all-silica sodalite

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In order to investigate the technical feasibility of crystalline porous silicates as hydrogen storage materials, the self-diffusion of molecular hydrogen in all-silica sodalite is modeled using large-scale classical molecular-dynamics simulations employing full lattice flexibility. In the temperature range of 700–1200 K, the diffusion coefficient is found to range from $1.6\cdot 10^{-10}$ to $1.8\cdot 10^{-9}\ \mathrm{m^2/s}$. The energy barrier for hydrogen diffusion is determined from the simulations allowing the application of transition state theory, which, together with the finding that the pre-exponential factor in the Arrhenius-type equation for the hopping rate is temperature-independent, enables extrapolation of our results to lower temperatures. Estimates based on mass penetration theory calculations indicate a promising hydrogen uptake rate at 573 K.

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I. INTRODUCTION

Porous, crystalline solids, with frameworks built up from TO_4 (T=Al,Si,Ge,P) tetrahedra, are attractive materials for the safe and efficient storage of hydrogen.[1–3] Porous solids for which the largest pore window openings have aperture dimensions similar to the kinetic diameter of hydrogen are especially interesting for hydrogen storage by means of encapsulation, i.e., trapping small gas molecules inside zeolitic cavities by changing the effective pore window opening to these cavities. This controlled encapsulation principle has previously been demonstrated in zeolites with respect to varying temperature,[4] and by application of an external force[5] to the material. The technical feasibility of such a storage method for any particular material depends on its maximum capacity and its maximum hydrogen uptake–release rate. In this study we concentrate on the latter property for the large void volume all-silica sodalite framework, and investigate, by means of molecular-dynamics (MD) simulations the diffusion rate of molecular hydrogen therein.

Previous MD studies of noble gases in sodalite have been performed with the diffusion of helium in all-silica sodalite at 300 K calculated to have a diffusion coefficient[6] of $3.8\cdot 10^{-9}\ \mathrm{m^2/s}$. With respect to hydrogen, Mitchell[7] has performed an MD-analysis on diffusion of hydrogen in zeolite NaA and in porous $Na_3ZnO(PO_4)_3$ at 773 K and found diffusion coefficients of around $7.0\cdot 10^{-8}$ and $8.0\cdot 10^{-9}\ \mathrm{m^2/s}$, respectively. In both these simulations the host–lattice is assumed to be rigid, which, especially in situations where the diameter of the largest pore is of dimensions similar to the diffusing molecule, can significantly affect the predicted magnitudes of the transport barriers.[8–11] For H_2 in all-silica sodalite we have explicitly demonstrated that this effect is significant[12] and, thus, in this study, the hopping rate of molecular hydrogen is calculated by means of molecular-dynamics calculations with a fully flexible all-silica sodalite framework. Simulations are performed at a number of temperatures throughout the region from 700 to 1200 K and from the determined hopping rate the self-diffusion coefficient is calculated based on transition state theory (TST). The large number of events sampled allows for statistical testing, validating our approach and the associated small estimated errors in our results. Finally, the diffusion coefficient is used to estimate the hydrogen uptake rate of all-silica sodalite at 573 K.

II. COMPUTATIONAL METHODOLOGY

All MD calculations have been performed using the computer code DLPOLY.[13] A full description of the employed interatomic potentials for the zeolite framework and their successful application are given in Refs. 14–19. The (Lennard-Jones) interactions between hydrogen and the oxygen and silicon atoms of the framework are derived and used in Ref. 20. A confirmation of the applicability of this combined set of potentials for calculating TST diffusion of hydrogen confined in flexible zeolitic frameworks is given in Ref. 12.

The hydrogen molecule is modeled as a centrosymmetric Lennard-Jones particle, which has proven to be a valid and accurate approximation with respect to extended representations in other studies.[12,21,22] We note that the zeolitic framework potentials employed have also been previously successfully used in a number of zeolitic MD simulations[23,24] further confirming their applicability to the present system. The cutoff for all interatomic potentials used was set to 13 Å.

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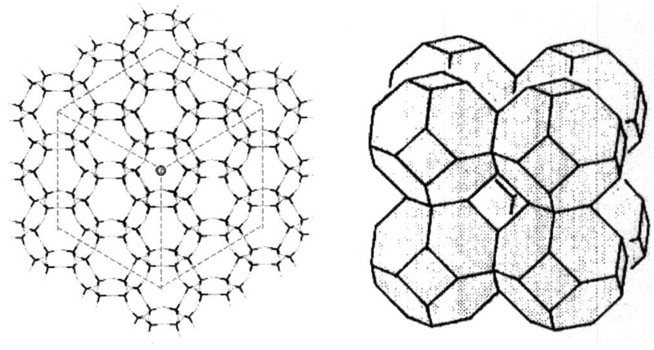

(A) **(B)**

FIG. 1. (A). Schematic representation of a 3×3×3 super cell system of all-silica sodalite, black is silicon and gray is oxygen, with one hydrogen molecule inside, represented by a gray sphere in the center. The dashed cube is added to show how the cubical unit cell is positioned in this representation of sodalite. (B). Schematic representation of a 2×2×2 super cell of sodalite in which the shape of a SOD-cage and the connectivity between the cages are clearly visible. The vertices are Si-atoms and the O-atoms are not shown but lie on the middle of an edge between two vertices.

Sodalite is modelled as a 3×3×3 unit cell system with periodic boundary conditions, $Si_{324}O_{648}$, employing no symmetry constraints, with one hydrogen molecule inside (cf. Fig. 1). The sodalite geometry is taken from the IZA database[25] and first energy-minimized in the computer code GULP,[26] with the Sanders[14] force field method at a constant pressure of 1 bar and with the BFGS optimization algorithm.[27] The optimized super-cell geometry has dimensions: $a, b, c = 26.9$ Å and $\alpha, \beta, \gamma = 90°$. The starting position for the hydrogen molecule was located in the center of an arbitrary sodalite cage.

For 800–1200 K, each MD simulation run had a duration of 2 ns, and for simulations at 700 K durations of 7, 8, and 10 ns were used, all including 0.2 ns of equilibration time and modeled with the NVT Evans ensemble.[28] For each temperature, enough simulations were performed to obtain at least 100 hops of the hydrogen molecule from one sodalite cage to an adjacent cage, resulting in corresponding cumulative simulation times of 7–64 ns. Optimization of the initial super cell, via energy-minimization using GULP,[26] allowing for variation in unit cell volume, showed that the volume did not change due to the introduction of one hydrogen molecule in the framework, confirming the validity of employing the constant volume ensemble. MD runs were performed at the temperatures: 700, 800, 900, 1000, 1100, and 1200 K with a time step of 0.001 ps.

The MD-output data was analyzed with an in-house hop counting program that assumed a rigid sphere inside each sodalite cage. Since the simulation was fully periodic, the partial cages on the outside of the super cell could be joined to make complete cages forming, accordingly, a total number of fifty-four complete cages (cf. Fig. 1). The program counted the hops between cages, listed the time of the hops and showed how the hydrogen moved through the framework. The geometrical state of the system is written every 0.5 ps to an output file, which is analyzed by this program. This time interval is small enough to keep track of the hydrogen molecule and a smaller sampling time would lead to extremely large memory requirements. All hops that happened within 1 ps of each other were checked manually. Immediate recrossing of the barrier was not counted as an event. If, after a hop, the H_2 molecule moved through the SOD-cage and then hopped through the opposing 6-ring in one straight line within 1 ps, this second hop was called a subsequent hop. This hopping behavior is listed in Table I and represents a form of correlation (*vide infra*).

The following equations are employed for the flux ($\boldsymbol{J}$) and the self-diffusion coefficient (D_{self}):

$$\boldsymbol{J} = -D_{\text{self}} \cdot \nabla c, \tag{1a}$$

$$D_{\text{self}} = \frac{\lambda^2}{6 \cdot \tau}. \tag{1b}$$

Equation (1a) is the general first law of Fick in which c stands for concentration. Equation (1b) is the Einstein equation for the self-diffusion coefficient valid in zeolites limited by energy barriers (the jump diffusion model).[29] Self-diffusion is defined as diffusion under conditions of low or constant concentration. The λ represents the shortest distance between two energy barriers (the hop length) and the τ represents the time interval between two hops. The hop length in sodalite is equal to half of the body diagonal of the unit cell, i.e., the shortest distance between the centers of two sodalite cages that are connected by a mutual 6 ring (cf. Fig. 1). For all-silica sodalite this is $0.5 \cdot \sqrt{3} \cdot 8.965 = 7.764$ Å.

Since the diffusion of hydrogen in small pore zeolites is limited by energy barriers that have to be overcome each time a molecule wants to move one step further, this diffusion can be modeled according to TST[29] which gives the following Arrhenius-type equation for the hopping rate in zeolites ($r[T]$):

TABLE I. Main results obtained from the MD-simulations.

Temperature [K]	Total simulation time [ns][a]	Total number of hops[b] [−]	Poisson error [%]	Total number of subsequent hops [−]	Hopping rate [hops/s]
700	63.8	100	10.0	2	$1.57 \cdot 10^9$
800	28.8	102	9.9	5	$3.54 \cdot 10^9$
900	21.6	146	8.3	6	$6.76 \cdot 10^9$
1000	14.4	126	8.9	5	$8.75 \cdot 10^9$
1100	10.8	133	8.7	4	$12.3 \cdot 10^9$
1200	7.2	128	8.8	2	$17.8 \cdot 10^9$

[a] Excluding equilibration time.

[b] Including the subsequent hops.

$$r[T]=\frac{1}{\tau}=A[T]\cdot e^{-\Delta E/k_B\cdot T}. \tag{2}$$

The exponential factor consists of the energy barrier (ΔE) divided by the Boltzmann constant (k_B) times the temperature (T). This is a Boltzmann-type factor indicating the probability of an event at a certain temperature. In our case, the event is the crossing of a 6-ring by a hydrogen molecule. As passage through the 6-ring is almost certainly the diffusion-limiting barrier for H_2 through any particular small pore zeolite structure, the diffusion rate can be expressed as the Boltzmann factor times a (possibly temperature dependent) pre-exponential rate factor $A[T]$.

Since the hopping rate is calculated as a function of temperature in the MD-simulations, the pre-exponential factor and the energy barrier can be determined by rewriting Eq. (2) in a linear form [see Eq. (3)] and plotting ln($r[T]$) versus $1/T$:

$$\ln(r[T])=\ln(A[T])-\frac{\Delta E}{k_B}\cdot\frac{1}{T}. \tag{3}$$

To obtain an estimate for the mass uptake rate of a sodalite crystal, the mass penetration theory[30,31] was applied. This theory states that the average hydrogen concentration inside a sphere ($\langle C_{H_2}\rangle$) can be calculated as a function of time (t), saturation concentration ($C_{\mathrm{H}_2}^{\infty}$), transport diffusion coefficient (D_trans), and sphere diameter (d) with Eqs. (4a) and (4b):[31]

$$\frac{\langle C_{H_2}\rangle}{C_{H_2}^{\infty}}=1-\frac{6}{\pi^2}\cdot\sum_{n=1}^{\infty}\frac{1}{n^2}\cdot\exp(-n^2\cdot\zeta), \tag{4a}$$

$$\zeta=\frac{4\cdot\pi^2\cdot D_\mathrm{trans}\cdot t}{d^2}. \tag{4b}$$

The derivative of Eq. (4a) gives the hydrogen flow (ϕ) into the crystal as a function of time as shown in Eq. (5):

$$\frac{\phi}{C_{H_2}^{\infty}}=24\cdot\frac{D_\mathrm{trans}}{d^2}\cdot\sum_{n=1}^{\infty}\frac{1}{n^2}\cdot\exp(-n^2\cdot\zeta). \tag{5}$$

Equations (4a) and (5) are only valid if the initial concentration in the sphere at $t=0$ equals to 0 and if the concentration at the surface of the sphere ($C_{\mathrm{H}_2}^{\infty}$) remains constant during the entire uptake period.[31]

The symbol D_trans stands for diffusion coefficient, however, it is a transport diffusion coefficient in contrary to the D_self in Eq. (1b) which is a self-diffusion coefficient. If the hydrogen concentration is low (i.e., if the hydrogen molecules are not interacting with each other) and the body is not affected by the mass uptake, the values of both diffusion coefficients are equal.[29] In other words, Eq. (4a) can only be applied with the diffusion coefficient obtained from Fig. 2 [in combination with Eq. (1b)] if the saturation concentration is low. A typical maximum could be one H_2 molecule per ten SOD cages (4.6×10^2 mol/m^3), because it is realistic to expect that the hydrogen molecules are not interacting with each other in that case.

The diameter of the all-silica sodalite crystals is set to 30 μm as has been found experimentally.[32] The outside area of a sodalite crystal consists of six square facets and eight hexagonal facets having a similar topology to a sodalite cage,[33] so it is reasonable to approximate the shape of a SOD crystal by a single sphere.

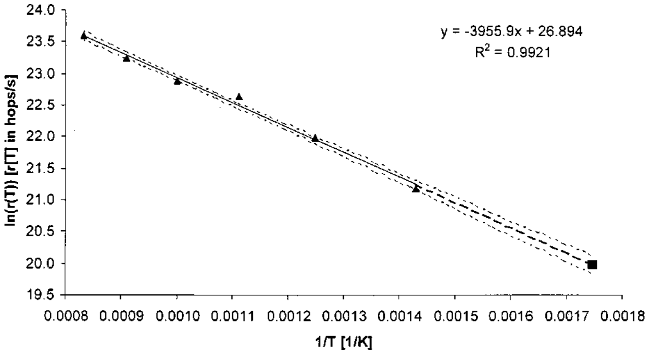

FIG. 2. Arrhenius plot of hydrogen diffusion in all-silica sodalite presented by the logarithmic value of the hopping rate vs the inverse of the temperature. The triangular point are the values obtained from the MD-simulations, the square point is the extrapolated point at 573 K, the line with long dashes is the extrapolated Arrhenius plot (equation given in the upper right corner of this figure), and the two lines with short dashes are the upper and lower confidence boundaries (68%).

By applying Eqs. (4a), (4b), and (5) for the calculation of hydrogen uptake, it is assumed that the mass uptake rate at the surface of the crystal is equal to the diffusion rate inside the crystal and that surface effects are, thus, not limiting. The mass uptake rate at the surface depends on the chemical structure and morphology of the crystal surface, which is currently unknown. However, even if this surface somewhat hinders the uptake of hydrogen into the crystal, it may be possible to use physical or chemical treatments to enhance the accessibility.

III. RESULTS AND DISCUSSION

Table I shows the main results obtained from the MD-simulations. As expected, the hopping rate increases with temperature. The reason that the chosen temperature range starts at 700 K is that the required computer time for calculation at lower temperatures becomes too large. The reason for the upper limit of 1200 K is the fact that sodalite starts decomposing above that value. Figure 2 gives the relation between ln($r[T]$) and $1/T$.

Figure 2 shows that the pre-exponential factor (A) is not significantly dependent upon temperature, therefore, it can be calculated by combining Eq. (3) with the equation of the line in Fig. 2 (upper right corner, obtained with the method of least squares), $A=\exp(26.894)=4.78\times 10^{11}\,\mathrm{s}^{-1}$. The error in this value is found to be $\pm 0.94\times 10^{11}\,\mathrm{s}^{-1}$. In the same way the energy barrier for diffusion (ΔE) is can be calculated, $\Delta E=3955.9\times k_B=3955.9\times 1.38\times 10^{-23}=5.5\times 10^{-20}\,\mathrm{J}(=32.9\pm 1.5\,\mathrm{kJ/mol})$.

The values of the hopping rate, the pre-exponential factor and the energy barrier are calculated based upon a limited number of cage hops. In order to determine the statistical error in these values, it is first tested if the hopping events can be approximated by a Poisson distribution, thus, if the inter-hop time intervals are distributed with a negative exponential function [cf. Eq. (6)]. The MD-output has shown that

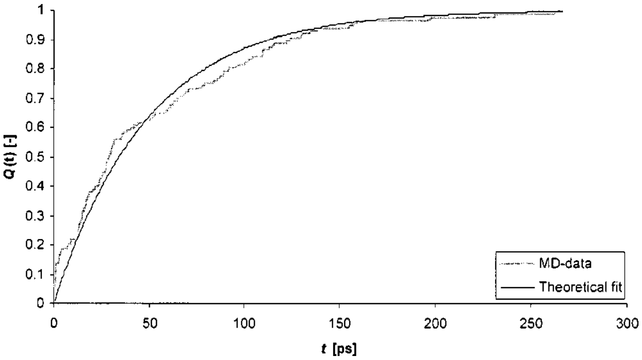

FIG. 3. The cumulative distribution of inter hop time intervals both from the MD-analysis of the self-diffusion of molecular hydrogen in all-silica sodalite at 1200 K and from Eq. (7) with $\lambda = 49$ ps.

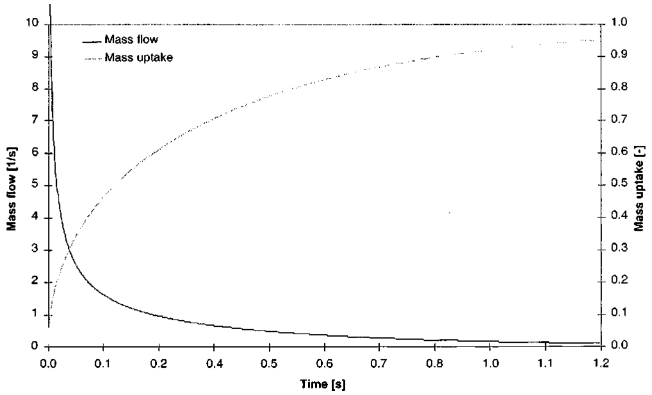

FIG. 4. Fractional mass uptake and mass flow into an all-silica sodalite crystal of 30 μm in diameter at 573 K as a function of time.

there exists a short-range correlation in the form of the so-called subsequent hops (cf. Table I). These subsequent hops form less than 5% of all hops and are, therefore, negligible, however, it is possible that there exist other correlations between the hops:

$$P(t) = 1/\lambda \cdot \mathrm{e}^{-t/\lambda}, \tag{6}$$

$$Q(t) = 1 - \mathrm{e}^{-t/\lambda}. \tag{7}$$

The probability $[P(t)]$ for a time interval (t) between two hops to have a certain value can be calculated with this equation. The value for the only constant (λ) in this equation can be estimated with the maximum likelihood principle. For a negative exponential distribution, it is the sum of all time intervals divided by their total number (n_t), $\Sigma_{i=0}^{i=n} t_i/n_t$. Both the time intervals at the beginning and the end of an MD-run are not taken into account because they are not complete. Therefore, the first hop in the MD-run is taken as the starting point for data sampling and the final hop as the end point.

To verify the assumption of a negative exponential distribution for the MD-data, the data from the MD-simulation at 1200 K is taken as a test case. The maximum likelihood estimation for the λ of the total data set of this simulation is 49.1 ps. If the cumulative distribution function of the MD-data is fitted to Eq. (7) [the cumulative equivalent of Eq. (6), with $Q(t)$ is the cumulative probability] with the Marquardt nonlinear fitting method (cf. Fig. 3), λ is determined to be 48.9 ± 0.9 ps. Since the previously mentioned maximum likelihood estimation of 49.1 ps falls within this value, this result indicates that the assumption of a negative exponential distribution is valid resulting in Poisson statistics for the number of hops in a given time interval.

Since the number of hops (N) in a certain time interval as determined with MD can be approximated by a Poisson distribution, the relative statistical error of this number can be calculated with $1/\sqrt{N} * 100\%$. This enables us to calculate the error in the hopping rate and, consequently, the error in diffusion coefficient (see Table I). Since the number of hops is always higher than 100, the error is always lower than 10%. In order to lower this error even further, a prohibitively demanding amount of computer time would be required.

The diffusion coefficient as a function of temperature can easily be obtained from Fig. 2 [cf. Eq. (1b)]. Values below 700 K are obtained via extrapolation (dotted line), which is possible if the pre-exponential factor in Eq. (2) is also independent of temperature outside the modelled temperature range. Arrhenius plots are generally valid for a large temperature range unless phenomena like phase changes occur. Such phenomena are highly unlikely to occur in our system at the temperatures studied in this paper and, therefore, Fig. 2 is also assumed to be linear in the extrapolated area. The errors in extrapolated values can be calculated with the method described in Ref. 34. For a 68% confidence interval (analogous to taking the standard deviation of a normal distribution as a measure of the error), the confidence boundaries for extrapolation are given in Fig. 2.

In order to get an idea of what a diffusion coefficient means in terms of hydrogen uptake rate, the mass penetration theory described in Sec. II is applied. For the loading temperature, the reported highest experimental value employed for storing hydrogen in alumina silica sodalite,[2] 573 K, is chosen. The diffusion coefficient at 573 K is $4.8 \times 10^{-11}\,\mathrm{m}^2/\mathrm{s}$ (cf. Fig. 2). The confidence boundaries show that the statistical error in this value due to extrapolation is 14%.

Figure 4 shows the fractional mass uptake, $\langle C_{H_2} \rangle / C_{H_2}^{\infty}$ $[-]$, and the accompanying mass flow into the crystal, $\phi / C_{H_2}^{\infty} [\mathrm{s}^{-1}]$, both as a function of time. If the saturation concentration is known, it can be multiplied with these values to give the absolute mass uptake and mass flow into the crystal. As said before, this figure is only valid in case of a low saturation concentration and no limiting surface effects.

Figure 4 shows that the mass uptake after 1.18 s is already 95% of the total mass uptake it needs to reach its saturation concentration (i.e., equilibrium with its environment). As said before, this value includes a number of assumptions, and should only be used as an indication of the mass uptake. However, this preliminary result is promising and make further experimental testing very interesting.

IV. CONCLUSIONS

The TST diffusion rate of hydrogen in all-silica sodalite is calculated from atomistic MD-simulations at six different temperatures. These calculations show that the pre-exponential factor in the Arrhenius equation does not significantly depend on temperature, allowing for linear extrapolation. Furthermore, the energy barrier for hopping has been found to be 32.9 kJ/mol. Statistical analysis showed that the hopping events could be approximated by a Poisson distribution and could, therefore, be considered as noncorrelated. This enabled us to do an error analysis of the results, showing that the error in the calculated diffusion coefficient at temperatures between 700 and 1200 K always lies below 10%. Calculating the mass uptake as a function of time at 573 K gives a mass uptake of 95% in 1.18 s for low saturation concentrations. This promising outcome makes sodalite an interesting candidate material for hydrogen storage.

[1] M. G. Nijkamp, J. E. M. J. Raaymakers, A. J. van Dillen, and K. P. de Jong, Appl. Phys. A: Mater. Sci. Process. **72**, 619 (2001).

[2] J. Weitkamp, M. Fritz, and S. Ernst, Int. J. Hydrogen Energy **20**, 967 (1995).

[3] A. M. Efstathiou, E. V. R. Borgstedt, S. L. Suib, and C. O. Bennett, J. Catal. **135**, 135 (1992).

[4] D. W. Breck, *Zeolites Molecular Sieves, Structure, Chemistry and Use*, 1st ed. (Wiley, New York, 1974), pp. 623–628.

[5] Th. Maschmeyer and J. C. Jansen, EP 1188477, 2002.

[6] M. J. Murphy, G. A. Voth, and A. L. R. Bug, J. Phys. Chem. B **101**, 491 (1997).

[7] M. C. Mitchell, J. D. Autry, and T. M. Nenoff, Mol. Phys. **99**, 1831 (2001).

[8] S. Nair and M. Tsapatsis, J. Phys. Chem. B **104**, 8982 (2000).

[9] P. Santikary and S. Yashonath, J. Phys. Chem. **98**, 9252 (1994).

[10] T. R. Forester and W. Smith, J. Chem. Soc., Faraday Trans. **93**, 3249 (1997).

[11] A. Bouyermaouen and A. Bellemans, J. Chem. Phys. **108**, 2170 (1998).

[12] A. W. C. van den Berg, S. T. Bromley, N. Ramsahye, and Th. Maschmeyer, J. Phys. Chem. B **108**, 5088 (2004).

[13] T. R. Forester and W. Smith, The DL_POLY_2 User Manual, CCLRC Daresbury Laboratory (1997).

[14] M. J. Sanders, M. Leslie, and C. R. A. Catlow, J. Chem. Soc., Chem. Commun. **1984**, 1271 (1984).

[15] N. J. Henson, A. K. Cheetham, and J. Gale, Chem. Mater. **6**, 1647 (1994).

[16] R. Grau-Crespo, E. Acuay, and A. R. Ruiz-Salvador, Chem. Commun. (Cambridge) **2002**, 2544 (2002).

[17] M. A. Camblor and M. J. Diaz-Cabanas, Chem. Mater. **11**, 2878 (1999).

[18] *Modelling of Structure and Reactivity in Zeolites*, 1st ed., edited by C. R. A. Catlow (Academic, San Diego, 1992), p. 38.

[19] D. W. Lewis and G. Sastre, Chem. Commun. (Cambridge) **1999**, 349 (1999).

[20] K. Watanabe, N. Austin, and M. R. Stapleton, Mol. Simul. **15**, 197 (1995).

[21] A. I. Skoulidas, D. M. Ackerman, J. K. Johnson, and D. S. Sholl, Phys. Rev. Lett. **89**, 185901 (2002).

[22] R. F. Cracknell, Phys. Chem. Chem. Phys. **3**, 2091 (2001).

[23] G. Sastre, C. R. A. Catlow, and A. Corma, J. Phys. Chem. B **106**, 956 (2002).

[24] L. Whitmore, B. Slater, and C. R. A. Catlow, Phys. Chem. Chem. Phys. **2**, 5354 (2000).

[25] http://www.iza-structure.org/databases

[26] J. D. Gale, J. Chem. Soc., Faraday Trans. **93**, 629 (1997).

[27] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).

[28] D. J. Evans and G. P. Morriss, Comput. Phys. Rep. **1**, 297 (1984).

[29] J. Karger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids* (Wiley, New York, 1992).

[30] W. J. Beek and K. M. K. Muttzall, *Transport Phenomena* (Wiley, New York, 1975).

[31] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 1st ed. (Clarendon, Oxford, 1997), p. 201.

[32] D. M. Bibby and M. P. Dale, Nature (London) **317**, 157 (1985).

[33] D. M. Bibby, N. I. Baxter, D. Grant-Taylor, and L. M. Parker, ACS Symp. Ser. **398**, 209 (1989).

[34] I. Miller, J. E. Freund, and R. Johnson, *Probability and Statistics for Engineers*, 3rd ed. (Prentice Hall, New Jersey, 1985), p. 333.