Effect of cation distribution on self-diffusion of molecular hydrogen in $\text{Na}_3\text{Al}_3\text{Si}_3\text{O}_{12}$ sodalite: A molecular dynamics study

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The diffusion of hydrogen in sodium aluminum sodalite (NaAlSi-SOD) is modeled using classical molecular dynamics, allowing for full flexibility of the host framework, in the temperature range 800–1200 K. From these simulations, the self-diffusion coefficient is determined as a function of temperature and the hydrogen uptake at low equilibrium hydrogen concentration is estimated at 573 K. The influence of the cation distribution over the framework on the hydrogen self-diffusion is investigated by comparing results employing a low energy fully ordered cation distribution with those obtained using a less ordered distribution. The cation distribution is found to have a surprisingly large influence on the diffusion, which appears to be due to the difference in framework flexibility for different cation distributions, the occurrence of correlated hopping in case of the ordered distribution, and the different nature of the diffusion processes in both systems. Compared to our previously reported calculations on all silica sodalite (all-Si-SOD), the hydrogen diffusion coefficient of sodium aluminum sodalite is higher in the case of the ordered distribution and lower in case of the disordered distribution. The hydrogen uptake rates of all-Si-SOD and NaSiAl-SOD are comparable at high temperatures (~ 1000 K) and lower for all-Si-SOD at lower temperatures (~ 400 K). © 2004 American Institute of Physics. [DOI: 10.1063/1.1808119]

I. INTRODUCTION

The safe and efficient storage of hydrogen presents one of the primary technical obstacles to be overcome before hydrogen may be used as a replacement for traditional fossil fuels. An inherently safe method of hydrogen storage is to adsorb it on, or throughout, a material so it is released very slowly in case of damage to the fuel tank. However, a large problem with adsorption can be the short cycle life of the adsorbent due to poisoning with impurities always present in the inflow of hydrogen. A possible route to avoid poisoning of the adsorbent is to employ size selective microporous materials such as zeolites either as a membrane for purification, or as an adsorbent for storage. The selective uptake and release of hydrogen in zeolites as adsorbents can be controlled relatively easily by altering temperature and pressure conditions¹ or by applying an external force on the material.²

Sodalite, in particular, seems to be a suitable zeolitic framework type for hydrogen purification and adsorption because of its large void volume (0.35 cc/cc) (Ref. 3) and the fact that it has pore aperture sizes suitable for hydrogen access, storage, and release. The apertures of sodalite are formed by T-O-containing rings, with four or six T atoms (T=Si or Al) which combine to form a close-packed network of cages, each containing 24 T atoms. The small four-membered rings present a very high-energy barrier for hydrogen to pass from one sodalite cage to another, and are thus practically inaccessible. The energy barrier of passing through a six-membered ring, however, can be overcome at

elevated temperatures and molecular hydrogen can pass through.¹ This indicates that the sodalite can be loaded at high temperature and pressure and that the hydrogen can be encapsulated by cooling at that pressure. Heating the zeolite up at a lower pressure allows the hydrogen to escape from the zeolite again.¹ This process will be highly selective since the six-membered ring is just large enough for hydrogen passage and H_2 is one of the smallest of all molecules. If sodalite is used as a membrane, the purification will also be very selective for the same reason.

In previous work,⁴ the diffusion of molecular hydrogen in all-Si-SOD was modeled in order to investigate the feasibility of sodalite as hydrogen encapsulating storage material. Although the modeled diffusion rate was promisingly high, all silica sodalite cannot be used in practice, because of the organic template around which the sodalite structure is built and which cannot be removed fully^{5,6} without destroying the structure. Therefore, in this study, as a more practical example, we investigate the self-diffusion of hydrogen in a flexible $3 \times 3 \times 3$ unit cell system of NaSiAl-SOD by means of classical molecular dynamics (MD) simulation at several temperatures. This type of sodalite can be made without an organic template by using the templating effect of the hydrated sodium cations. If this sodalite is dried under vacuum conditions an "empty" structure can be obtained.⁷

The sodalite structure consists of a dense body-centered cubic (bcc) lattice packing of one type of cage (4^66^8).⁸ From x-ray diffraction (XRD) structural refinement,⁹ it has been found that each sodalite cage has eight equally likely positions for the cations, being the eight six-ring centers.

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TABLE I. Parameters for the Buckingham potentials.

Bonding atoms	A (eV)	ρ (Å)	C (eV Å ⁶)	Reference
O-Si	1283.907	0.320 52	10.66	13
O-Al	1460.300	0.299 12	...	14
O-Na ⁺	1226.840	0.306 50	...	14
O-O	22 764.000	0.149 00	27.88	13
Na ⁺ -Na ⁺	7895.400	0.170 90	...	14

Because of the negatively charged aluminum atoms in the NaSiAl-SOD framework, six out of eight six-rings per cage are occupied by a (singly charged) cation. For a long time it was unknown how the exact distribution of the cations over the structure is organized, due to the difficulty of performing single crystal XRD on the available small-sized dehydrated NaSiAl-SOD crystals. A few years ago, however, Campbell *et al.*⁷ performed variable temperature synchrotron x-ray powder diffraction and by combining these measurements with computational modeling,¹⁰ they found that at temperatures above ~ 535 K the cations were not ordered and below 535 K a certain cation ordering was present.

Our present computational study investigates the NaSiAl-SOD system with two extremes of cation distribution.

(i) A fully ordered cation distribution with open channels in the (111) direction, the energetically most favorable configuration of the cations for the cubic unit cell.¹⁰

(ii) A disordered distribution of cations with no specific channels.

We concentrate our investigation on the effect that cation ordering has on the hydrogen diffusion coefficient throughout the NaSiAl-SOD framework. The calculated energy barriers and hydrogen diffusion coefficients for NaSiAl-SOD are also compared with our previous calculations⁴ on all silica sodalite.

II. COMPUTATIONAL METHODOLOGY

All MD calculations have been performed using the computer code DLPOLY.¹¹ A full description of the interatomic potential forms for the zeolite framework with hydrogen inside is given in Ref. 12. The empirical parameters employed in the current investigation are given in Tables I–III. The cut-off for all interatomic potentials used was set to 13 Å unless stated otherwise.

The force field employed to calculate the interatomic interactions between the framework atoms of the zeolite is given in Refs. 13 and 14. This force field has been proven to reproduce very accurately various zeolite structures,^{15–17} their relative energies¹⁸ and zeolite vibrational properties¹⁹ in

TABLE III. Parameters for the Lennard Jones potentials.

Interacting atoms	ϵ (eV)	σ (Å)	Reference
Si-H ₂	0.002 254 531	1.8175	22
Al-H ₂	0.002 284 633	1.9870	22
O-H ₂ ^a	0.006 773 687	2.8330	22
O-H ₂ ^b	0.005 270 509	2.8330	22
Na ⁺ -H ₂	0.002 372 648	2.3520	22

^aFor zeolites that contain Si and Al.

^bFor zeolites that only contain Si.

energy minimization calculations. Additionally, it has been shown to be suitable for the molecular dynamics simulation of diffusion along inner and outer zeolite surfaces and pores.^{20–21} We have found in previous studies that it is essential to model the framework in a fully flexible manner in order to accurately model the activated diffusion process.^{4,12} Alternatively, one could decide to keep the framework rigid; however, our calculations have indicated that this would artificially increase the energy barrier for diffusion by $\sim 20\%$ in the case of NaAlSi-SOD, due to the total loss of six-ring flexibility. Furthermore, it would mask any important influences of cation distribution on six-ring flexibility and, thus, diffusion rates (*vide infra*).

The (Lennard Jones) interactions between hydrogen and all framework atoms (Na⁺, Si, Al, and O) are derived from experimental data of gas adsorption on zeolites by Watanabe *et al.*²² In this model, 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 molecular representations of H₂ in other studies.^{12,23–24}

Sodalite is modeled as a $3 \times 3 \times 3$ unit cell system with periodic boundary conditions, Na₁₆₂Si₁₆₂Al₁₆₂O₆₄₈, employing no symmetry constraints, with one hydrogen molecule inside. The sodalite geometry is taken from the IZA database.⁸ Since this geometry is based on experimental measurements on sodalite filled with water and NaCl,⁹ the framework was first energy-minimized in the computer code GULP (General Utility Lattice Program),²⁵ employing the above force field at a constant pressure of 1 bar with the Broyden, Fletcher, Goldfarb and Shanno (BFGS) based optimization algorithm,²⁶ in order to get a geometry that gives a better representation of the empty structure. The optimized supercell geometry has dimensions: a , b , $c = 27.59$ Å and α , β , $\gamma = 90^\circ$. The starting position for the hydrogen molecule was located in the center of an arbitrary sodalite cage.

MD simulations were performed at 800, 900, 1000, 1100, and 1200 K with the *NVT* Evans ensemble²⁷ using a time step of 0.001 ps. This temperature range is chosen based upon practical consideration of the stability of sodalite and the duration of the simulations. Optimization of the initial supercell via energy minimization, 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. The simulation time was chosen long enough to include at least 100 hops in order to ensure a statistical error of $< 10\%$ (cf. Table IV).

TABLE II. Parameters for the three-body potentials.

Atoms in angle	k2 [eV rad ⁻²]	q_0 (°)	Cut-off distances (Å)	Reference
O-Si-O	2.097 24	109.47	1.8, 1.8, 3.2	13
O-Al-O	2.097 24	109.47	1.8, 1.8, 3.2	14

TABLE IV. Main results obtained from the MD simulations for (a) the fully ordered cation distribution and (b) the disordered cation distribution.

	Temperature (K)	Total simulation time ^a (ns)	Total number of hops ^b (–)	Poisson error (%)	Total number of subsequent hops (–)	Total number of rapid recrossings (–)	Hopping rate (1×10^{10} hops/s)
(a)	800	25.2	164	7.8	3	4	0.65
	900	14.4	138	8.5	5	2	0.96
	1000	10.8	114	9.4	7	2	1.06
	1100	9.0	129	8.8	5	3	1.43
	1200	7.2	107	9.7	2	3	1.49
(b)	800	23.8	120	9.1	0	1	0.50
	900	14.8	104	9.8	0	1	0.70
	1000	9.8	109	9.6	1	3	1.11
	1100	9.8	118	9.2	0	1	1.20
	1200	9.8	172	7.6	1	5	1.76

^aExcluding equilibration time.^bIncluding the subsequent hops and excluding rapid recrossings.

During the simulations occasionally a cation hopped from one adsorption spot (i.e., six-ring) to another. This spontaneous cation diffusion is a rare relatively high-energy event of which the rate is negligible in relation to the hydrogen diffusion rate in sodalite. Significant cation mobility at lower temperatures has been observed in atomistic MD simulations but to our knowledge only when induced by polar molecules, e.g., water and chloroform,²⁸ not present in our simulated model. The fact that the cations are effectively localized over the length of our simulations allows us to investigate the effect of cation ordering at higher temperatures (800–1200 K) and, thus, within more practicable computational time scales, and also to predict likely effects at lower temperatures (~ 573 K).

The MD-output data was analyzed with an in-house hop counting program.⁴ All hops that happened within 1 ps of each other were checked manually. A few rapid recrossing events were observed (see Table IV); however, these were not counted as a hopping event. If, after a hop, the H₂ molecule moved through the SOD cage and then hopped through the opposing six ring in one straight line within 1 ps, this event was called a subsequent hop (see Table IV). These subsequent hops are taken explicitly into consideration when calculating the diffusion coefficient [see Eq. (4)].

The transition-state-theory-based method to calculate the self-diffusion coefficient D based on a random walk model for hydrogen in sodalite from the hopping rate ($r[T]$) obtained from the MD data and the mass penetration method to translate this diffusion coefficient into a hydrogen uptake are described in Ref. 4. The relevant equations are repeated below,

$$D = \frac{\lambda^2}{2 \cdot \dim} r[T] = \frac{\lambda^2}{2 \cdot \dim} A[T] e^{-\Delta E/k_B T}, \quad (1)$$

$$\frac{\langle C_{H_2} \rangle}{C_{H_2}^\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \frac{4\pi^2 D \cdot t}{d^2}\right). \quad (2)$$

In Eqs. (1) and (2), the λ represents the hopping length ($0.5 \times \sqrt{3} \times 9.197 = 7.96$ Å), $\dim$ represents the dimension of the random walk ($\dim = 1, 2$ or 3), $A[T]$ the pre-exponential

rate constant, ΔE the energy barrier for diffusion, k_B the Boltzmann constant, T the temperature, $\langle C_{H_2} \rangle$ the average hydrogen concentration in the crystal, $C_{H_2}^\infty$ the hydrogen saturation concentration, d the crystal diameter, and t the time.

If a sodalite six-ring is occupied by a cation, a hydrogen molecule cannot pass through that ring (pore blocking^{29,30}). As a result, hydrogen in the fully ordered system can only move along the channel in the (111) direction. In other words, the hydrogen moves according to a one-dimensional random walk for which Eq. (1) writes as

$$D = \frac{\lambda^2}{2} r[T] = \frac{\lambda^2}{2} A[T] e^{-\Delta E/k_B T}. \quad (3)$$

In order to correct for subsequent hops, the equation is extended as³¹

$$D = \frac{1}{2} (r_{1 \rightarrow 2}^{el} \lambda^2 + 4 r_{1 \rightarrow 3}^{el} \lambda^2) \quad (4)$$

with $r_{1 \rightarrow 2}^{el}$ = elementary hopping rate of the hops from a cage 1 to one of its direct neighboring cages 2 (i.e., normal hops), $r_{1 \rightarrow 3}^{el}$ = elementary hopping rate of the hops from cage 1 to cage 3 in the second shell surrounding cage 1 (i.e., subsequent hops).

For the calculation of hydrogen diffusion in the disordered system, the simple random walk model [Eq. (1)] cannot be applied any more and the more general form given by Eq. (5) is necessary:³²

$$D = \frac{\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle}{2 \cdot \dim \cdot t}. \quad (5)$$

Since long term movement in all directions is possible in the disordered system, the diffusion is three-dimensional ($\dim = 3$). In order to obtain the mean square displacement per unit of time at a certain temperature T , $\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle / t$, the following procedure is applied: First we distinguished between eight different cage types based on accessibility, i.e., cage type 1 had one open six-ring, cage type 2 had two open six-rings, etc. It was not possible to make a further discrimination between different cation arrangements in the

cage due to the limited amount of the MD data; however, it is reasonable to assume that the exact geometrical arrangement of the openings has a negligible effect on the elementary hopping rate associated with passage through an individual ring. Second, the average residence time per cage type at T , as determined from the MD data, was used as input for an in-house path-sampling program which generates N pathways ($N=10^4$) with a fixed travel time on the bcc lattice of cage centers (corresponding to $32 \times 32 \times 32$ unit cells with periodic boundary conditions). The cations were represented as a cubic lattice of obstacles, the cation distribution being random (fill fraction 3/4) and frozen while generating the path. The average of the squared path lengths versus t gives a linear graph, which is analyzed with the method of least squares to find the slope equalling the mean square displacement per unit of time. Since subsequent hops were effectively absent in the disordered system during the MD simulations no correction was necessary.

Since quantum corrections are sometimes necessary even at relatively high temperatures when dealing with the activated diffusion of light molecules,^{33,34} this correction factor is calculated at 800 K, the lowest temperature employed in our calculations, with the help of Eq. (6) (Ref. 33) (m = mass of H_2 molecule):

$$r[T]_{corrected} = \frac{1}{\alpha} r[T]$$

with

$$\alpha = \exp\left(-\frac{\hbar^2}{24m(k_B T)^2} [|U''_{top}| + |U''_{bottom}|]\right). \quad (6)$$

The values for the second derivatives of the potential energy at the top, $|U''_{top}|$, and the well, $|U''_{bottom}|$, of the energy barrier for diffusion are estimated from the energy barrier plot given in Ref. 12. The latter is set to zero, because the bottom of the well is effectively flat, and the former is obtained by fitting a second-order polynomial to the top and taking its second derivative, -6.9636 J/m^2 . The correction factor α at 800 K is 0.992, showing that the quantum effects make a difference of $<1\%$ and are, thus, negligible at the simulated temperatures. It is interesting to note, however, that such quantum effects already become relevant ($>5\%$) at temperatures lower than 320 K.

III. RESULTS AND DISCUSSION

A. Comparing H_2 diffusion in NaSiAl-SOD for fully ordered and disordered cation distributions

Table IV shows the main results obtained from the MD simulations and Fig. 1 gives the accompanying Arrhenius plots of the hopping rates for the fully ordered and disordered cation distributions in NaSiAl SOD. The hopping time intervals were found to be exponentially distributed to a high degree of accuracy for all MD simulations (Poisson statistics, see also Ref. 4), therefore, the errors in all values of the hopping rate can be calculated with $100\%/\sqrt{N}$ (with N = number of hops). These errors are given in Table IV and are represented in Fig. 1 by means of error bars. Since these

FIG. 1. Arrhenius plots of the H_2 hopping rate in fully ordered (triangles, black error bars) and disordered (squares, gray error bars) distribution of cations in NaSiAl-SOD.

bars are only overlapping in the temperature area where the plots are crossing (around $T=1100 \text{ K}$) it can be concluded that both Arrhenius plots are really different.

The method of least squares is used to fit both Arrhenius plots to straight lines which is shown to be a good approximation in both cases (see R^2 values given in Fig. 1). Therefore, the energy barriers for hopping and the pre-exponential rate factors [cf. Eq. (1)] are temperature independent and equal to $16.66 (\pm 1.87)$ and $24.26 (\pm 2.23) \text{ kJ/mol}$ and 8.27×10^{10} ($\pm 1.91 \times 10^{10}$) and 18.94×10^{10} ($\pm 5.23 \times 10^{10}$) s^{-1} for fully ordered and disordered cation distributions, respectively.

The reason for the significant difference in hopping energy barrier, which is mainly responsible for the large difference in hopping rate in the interesting temperature region below 1000 K, could be the difference in the flexibility¹² of the frameworks due to the difference in cation ordering. The framework flexibility is investigated by calculating the phonon modes of the ordered and disordered system using GULP (Ref. 25) based on the force fields described previously.

The result is given in Fig. 2 which shows that although the phonon modes are rather less well defined (peak broadening) for the disordered cation system compared to the sodalite containing an ordered cation distribution, the features in both spectra match one another very well in the regions above 800 cm^{-1} and below 530 cm^{-1} . For the region $530\text{--}800 \text{ cm}^{-1}$, however, the features in each spectrum ap-

FIG. 2. Phonon modes of the fully ordered (gray line) and disordered (black line) NaSiAl-SOD system (without H_2) calculated in GULP (Ref. 25). The supercell geometry and employed force field were the same as used for the MD simulations. The resolution is 10 cm^{-1} .

FIG. 3. Scheme of a sodalite six ring; side view (left) and top view (right). The gray spheres represent oxygen atoms and the black spheres represent T atoms ($T=\text{Si}$ or Al). The dashed lines connecting the oxygen atoms that lie in the planes above and below the silicon plane, form two virtual triangles. These dashed lines are a guide to the eye.

pear to be shifted or even anti-aligned with respect to each other. From other studies it is known that the six-ring bending modes are located in this region,³⁵ and thus it is interesting to take closer look at the effect of hydrogen accessibility through a six-ring for both cation distributions. Figure 3 gives a detailed scheme of an accessible SOD six-ring viewed from two different angles. The six oxygen atoms that form an open six-ring can be divided into two triplets forming virtual triangles lying on opposite sites of the ring (this oxygen alternating structure has been verified by XRD studies of sodalite⁹). As the hydrogen passes through the centers of both oxygen triangles on its way through the six-ring the energy barrier height is determined by the smallest triangle area. Since the six-ring possesses some flexibility, the smallest triangle can expand a little, thus, reducing the barrier for passage. This is illustrated in Fig. 4 for both systems.

Figure 4 gives the six-ring opening and total system energy change *versus* H_2 position in relation to the six-ring for H_2 trajectories passing through the lowest energy barriers for diffusion, for a six-ring in both a fully ordered and disordered cation distributed framework (for a full description of this optimization method see Ref. 12). These lowest barriers belong to a H_2 trajectory passing straight through the middle of the cage and the middle of the six-ring.

The average triangle areas are approximately the same for both cases as would be expected, because the overall size of the six-ring is not influenced by the cation distribution. Furthermore, the average triangle areas are at their maximum when the hydrogen is positioned in the center of the six-ring which was also to be expected based on the short distance repulsive interaction between H_2 and the six oxygen atoms. It is more interesting to look at each triangle separately. For the fully ordered cation distribution the triangle areas are equal and respond to H_2 passage in exactly the same way, thus, showing perfect ring symmetry; i.e., if hydrogen passes through triangle 1, this triangle is stretched while triangle 2 is compressed due to ring connectivity and when H_2 passes

through triangle 2 the opposite occurs. The triangle areas of the six-ring with a disordered cation environment, however, behave significantly different, thus, indicating six-ring asymmetry.

Figure 4 shows that the maximum system energy values, 7.76 (top) and 8.55 (bottom) kJ/mol, correspond to a H_2 molecule in the center of the six-ring. The zero energy is equal for both systems and corresponds to H_2 in its adsorption spot in front of the six-ring. Therefore, the difference in barrier is caused by the difference in system energy with H_2 positioned at the center of the six-ring. This energy is higher for the six-ring of the disordered cation system, because this ring is, due to its asymmetric environment, less able to adapt its shape to the presence of the H_2 molecule. In other words, the six-ring of the ordered cation system is more flexible and, thus, better accommodates the hydrogen molecule leading to a greater dampening of the energy profile. The difference in six-ring symmetry causes the barrier belonging to the most favorable trajectory through the six-ring already to increase by 10% for cation disorder. This means that for less favorable H_2 trajectories the difference in energy barrier will even be larger, in agreement with the results obtained from the MD simulations.

The Arrhenius plots of the diffusion coefficients of hydrogen in fully ordered and disordered NaSiAl-SOD and in all-Si-SOD are given in Fig. 5. Figure 5 shows that the slopes of the Arrhenius plots belonging to ordered and disordered NaSiAl-SOD differ in the same way as the plots of the hopping rates. As the hopping rate and diffusion coefficient are interdependent, this strongly indicates that the reason for this difference again lies with the respective difference in framework flexibility.

Second, the order of magnitude is very different for both diffusion coefficients. This is mainly caused by the nature of the self-diffusion in both systems. In the case of ordered NaSiAl-SOD , the hydrogen moves according to a one-dimensional random walk through the straight (111) channels. This increases the diffusion with a factor 3 [see Eq. (1)]. Additionally, the diffusion coefficient in case of the ordered system is increased with about 7% due to the occurrence of subsequent hops in this system [see Eq. (4)]. In disordered NaSiAl-SOD , the hydrogen moves according to a three-dimensional random walk on the level of the crystal [see Eq. (5)], however, with the constraint that only a limited number of randomly distributed openings are accessible in each cage (typically 1–4). This constraint leads to a strong lowering of the mean square displacement per unit of time and, thus, of the diffusion coefficient with respect to the fully unblocked three-dimensional system. For example, diffusion into a cage with only one opening will always lead to a net displacement of zero as soon as it moves out again. Diffusion into a cage with two openings gives in 1/2 of all follow-up events a net displacement of zero (i.e., a slow recrossing), while if all cage openings are accessible (totally unblocked system), the chance on a net zero displacement is only 1/8.

In the actual NaSiAl-SOD material it is not known how

FIG. 4. Relation between six-ring opening and total system energy for the passage of H₂ through the six ring of a fully ordered system (top) and a disordered system (bottom). The x axis gives the position of the hydrogen molecule on its trajectory through the six ring and the vertical line between 2 and 3 Å indicates the position of the six-ring center. The filled black circles indicate the total system energy (right y axis). The light gray triangles indicate the surface areas (left y axis) of the two virtual triangles shown in Fig. 3. The dark gray diamonds indicate the average triangle area. The lines are a guide to the eye.

the cations are distributed inside the sodalite crystal at our simulated temperatures. Although the presence of straight channels, as in our fully ordered model, seems unlikely at high temperatures, it is not unreasonable to suppose that some local ordering is present. The diffusion results presented in Fig. 5 can, therefore, only be used to fence the area within which the real diffusion rate lies. Furthermore, we know from Refs. 7 and 10 that the NaSiAl-SOD cation distribution becomes more ordered at temperatures below 535 K. If it is assumed that the Arrhenius plots in Fig. 5 are still valid in this temperature region, the upper Arrhenius line is valid for that system, meaning that the sodalite becomes more accessible below 573 K (i.e., a change of slope in the experimental Arrhenius plot is expected there).

In order to check our predictions with experiment it would be necessary to find the exact self-diffusion rate. In principle this could be measured with, for example, solid state NMR.³² The reason that this has not been done yet lies probably in the fact that it is very difficult to remove all the water from the very hydrophilic framework⁷ and to keep it dehydrated during measurement.

B. Comparing NaSiAl-SOD and all-silica SOD

The diffusion coefficient of all-Si-SOD is also given in Fig. 5 (gray line).⁴ Since in all-Si-SOD all six-ring windows are accessible, the diffusion coefficient can be calculated with Eq. (1) with $\text{dim}=3$. The slope of the Arrhenius plot of

FIG. 5. Arrhenius plots of the self-diffusion coefficients of hydrogen in fully ordered NaSiAl-SOD (black squares), disordered NaSiAl-SOD (black diamonds) and all-Si-SOD (gray triangles). The corresponding equations and least squares fits are given on the right end of the graphs.

all-Si-SOD is much steeper than that of NaSiAl-SOD, showing that the energy barrier for hopping is much higher for all-Si-SOD. This is caused by the difference in six-ring pore window opening; in NaSiAl-SOD it is larger ($22.1 \text{ \AA}^2$ versus $20.4 \text{ \AA}^2$) due to the larger Al–O bonding length [$1.74 \text{ \AA}$ versus $1.61 \text{ \AA}$ for Si–O (Ref. 10)].

The difference in hydrogen loading rate at low hydrogen saturation conditions can be quantified by applying Eq. (2). Table V gives the comparison at different temperatures.

Table V shows that at high temperatures, the uptake time in all-Si-SOD lies in the same order of magnitude as that of ordered NaSiAl-SOD. Compared to disordered NaSiAl-SOD, the more likely cation distribution at high temperatures, all-Si-SOD has a significantly quicker H_2 uptake. At lower temperatures ordered NaSiAl-SOD is the more likely structure and compared to that all-Si-SOD becomes increasingly slower with decreasing temperature. For example, at 573 K the time needed to obtain a 95% hydrogen saturated SOD crystal of $30 \text{ }\mu\text{m}$ in diameter is 1.2 s for all-Si-SOD,⁴ 0.1 s for ordered NaSiAl-SOD and 3.4 s for disordered NaSiAl-SOD.

Due to the large difference in slopes, the Arrhenius plots cross at certain temperatures if one assumes that the plots stay linear also outside the simulated temperature area. From the equations in Fig. 5, it can easily be found that the all-Si-SOD plot crosses the ordered NaSiAl-SOD plot at 8210 K and the disordered NaSiAl-SOD plot at 345 K. The former crossing is not interesting because sodalite cannot exist at

TABLE V. Ratios between the uptake times of all-Si-SOD, and ordered and disordered NaSiAl-SOD at different temperatures.

Temperature ^a (K)	All-Si-SOD	Ordered NaSiAl-SOD	Disordered NaSiAl-SOD
1200	3	1	20
1100	3	1	21
1000	4	1	22
900	5	1	23
800	6	1	25
573	12	1	34
345	69	1	69

^aThe values for the two extrapolated temperatures, 573 and 345 K, can only be used to get an indication of the ratios, because extrapolation errors for D_{self} are already rather large at these temperatures ($>25\%$).

such temperatures, however, the latter one is, because combining this information with the knowledge that at lower temperatures, the NaSiAl-SOD system is more ordered and thus has an Arrhenius plot that lies closer to the upper limit, leads to an important technical consequence: if sodalite is used as a membrane for H_2 purification (at reasonably low temperatures) it would be better to use NaSiAl-SOD, because of the higher diffusion rate (see Table V). Used as a H_2 storage material, however, it would be better to use all-silica SOD, because it loads with a rate comparable to NaSiAl-SOD at high temperatures but retains H_2 via encapsulation more strongly at lower temperatures.

IV. CONCLUSIONS

The diffusion of molecular hydrogen in $\text{Na}_3\text{Al}_3\text{Si}_3\text{O}_{12}$ sodalite in the temperature range of 800–1200 K depends on the cation distribution in the framework. A more ordered distribution leads to a higher framework flexibility and, therefore, to a lower energy barrier for cage hopping. Furthermore, the occurrence of correlated hops in case of the ordered distribution and the difference in nature of diffusion lead to a much larger diffusion coefficient for the ordered cation distribution than for the disordered distribution. Compared to all-silica sodalite, NaSiAl-SOD has a lower energy barrier for diffusion, because of its larger pore window opening. However, the diffusion rates are very comparable at high temperatures and only become significantly different at lower temperatures, where for NaSiAl-SOD the uptake rate is higher than for all-Si-SOD.

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