

Adsorption of Selenium Wires in Silicalite-1 Zeolite: A First Order Transition in a Microporous System

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A tight binding grand canonical Monte Carlo simulation of the adsorption of selenium in silicalite-1 zeolite is presented. The calculated adsorption-desorption isotherms exhibit characteristic features of a first order transition, unexpected for adsorption in a microporous system with pore size of the order of 0.5 to 0.6 nm. We analyze this behavior as a result of the favored twofold coordinated chain structure of selenium that grows inside the complex three-dimensional microchannel network of silicalite. This analysis is confirmed by simpler calculations of a lattice gas-type model.

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Confining semiconductors in a porous matrix is one possible way to obtain nanostructured materials with potentially original properties. The nanometric size of the confined material as well as the possibility to incorporate guest elements in a well organized matrix such as a zeolite structure is one reason for the ever-growing interest in the field. The possibility to study real systems in reduced dimensionality is a second, more fundamental motivation. Recent experimental work has been devoted to the study of Se confined inside different types of zeolites [1–4]. It shows that it is possible to incorporate small molecules or chains of Se into various microporous materials (cancrinite, AlPO₄-5 or cage zeolites) with pore sizes or windows ranging from 5 to 7 Å. The structure of the adsorbed phase of Se has been studied by x-ray absorption [5,6] or Raman spectroscopies [3,4] in various confining matrices. The choice of Se as a guest element derives from the expected optoelectronic properties as well as from the low melting point of this element ($T_m = 490$ K) that makes it possible to incorporate it in the porous matrix in a fairly simple way.

This paper presents a computer simulation study of the adsorption of Se into silicalite. The interest of this study is twofold. First, silicalite presents a network of interconnected straight and zigzag microchannels of about 5 Å in diameter. These channels are large enough to incorporate single Se chains, and the channel intersections are expected to induce changes in the electronic structure, as compared to that of crystalline Se, by modifying the coordination of the sites at the intersections. Indeed, onefold (Se^I) or threefold (Se^{III}) coordinated defects relative to the ideal chain structure of Se modify [7] the electronic structure, ultimately leading to the metallic behavior observed in the liquid phase, at high temperature and high pressure [8]. A second interesting aspect is the sorption process itself. Our results suggest that the incorporation of Se which

has a well known preference to adopt twofold coordinated chain structures in the three-dimensional network of the microchannels available for adsorption presents the characteristic features of a first order phase transition. In the present paper we focus on this second point.

The central issue in the numerical study of the adsorption of Se in a zeolite is to describe accurately the directional covalent bonding of Se. The interactions between Se atoms are treated within the semiempirical tight binding framework described in Ref. [7]. It describes the formation of the chemical bond in a minimal *sp* basis set, neglecting charge transfers and self-consistency. The total energy of the Se subsystem is the sum of three contributions: an attractive band structure term, a pairwise additive empirical repulsive term, and a longer range van der Waals attractive term. The fourth moment approximation used here is the simplest that yields the most important features of the bonding of Se: angular dependence of the bonding, twofold coordination favored for Se allowing the possibility of undercoordinated (Se^I) or overcoordinated (Se^{III}) defects with reasonable energy differences between them. The resulting total energy model for Se was shown to be valid for the computer simulation of disordered phases: the results compare favorably with both experimental [7] and *ab initio* [9] determinations of the structure of the liquid and are in qualitative agreement with quantum chemistry calculations for small molecules [10]. Moreover, the liquid-vapor coexistence curve calculated by a Gibbs ensemble Monte Carlo [11] technique are in agreement with the experimental data [12] and yield a critical temperature of 1800 ± 100 K [13], to be compared with the experimental $T_c = 1903$ K.

In the case of “neutral” zeolites (e.g., silicalite, AlPO₄-5) the interactions of Se with the SiO₂ matrix are weak. *Ab initio* calculations of the total energy of 42 selenium atoms confined into one unit cell of silicalite (96 Si

and 192 O atoms) were performed using the ABINIT program [14]. The 42 Se atoms were relaxed using the semi-empirical energy model, and the zeolite structure was fixed. Figure 1 is a view of the structure (42 Se atoms incorporated in one unit cell of silicalite) on which the calculations were performed. A relatively small energy cutoff (10 Ryd) was taken, owing to the very large number of atoms to be treated. The pseudopotentials were taken from Troullier and Martins [15]. The interaction energy between Se and silicalite is equal to 0.412 eV/Se atom, clearly in the range of van der Waals interactions, although the local density approximation used here is not well suited to give an accurate estimate of such kind of interactions which involve excited electronic states. We assume that this interaction energy does not depend on the state of coordination of Se and that the SiO₂ matrix remains rigid throughout the adsorption process, and consequently we use a PN-type potential function [16]. The dispersion and induction parts of the adsorption energy (Se-O and Se-Si interactions) are obtained assuming that Se atoms have a polarizability of 4.15 Å³ [17] and an effective number of electrons equal to 5.61. The Se-O and Se-Si repulsive contributions (Born-Mayer terms) are taken equal to those for Kr/silicalite interaction since Se and Kr have the same van der Waals radius (1.85 Å) [18]. With this model the interaction energy of the 42 Se atoms with the silicalite cell is equal to -0.208 eV/Se atom. The larger magnitude of Se-Se (of the order of -2.2 eV/Se atom) as compared to Se-silicalite interactions indicates that the accuracy in the description of the latter (in particular, concerning the description of the repulsive terms) is not essential to capture the physics of the adsorption process. Most of our results concerning the thermodynamics of the adsorption would hold true using a smooth repulsive confining potential.

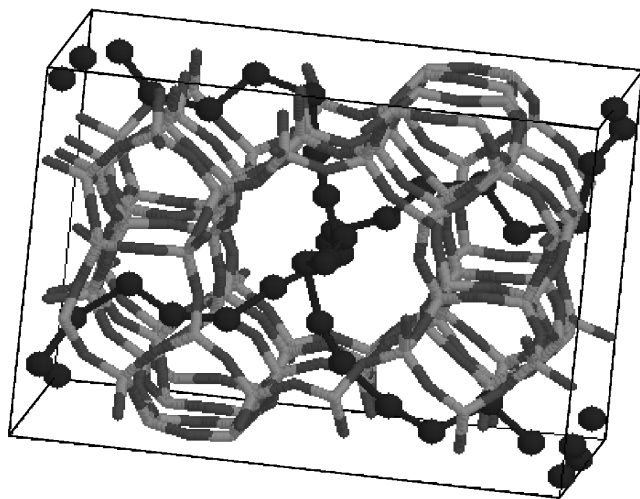


FIG. 1. A view of one unit cell of silicalite (wireframe structure) containing 42 Se atoms (in black). All Se atoms are two-fold coordinated. The central void is a straight channel; zigzag channels are seen from the side.

In the grand canonical ensemble, the independent variables are the chemical potential (μ), the temperature (T), and the volume of the simulation box [19]. The chemical potential of the bulk phase is related to the temperature and the bulk pressure. In the present instance, the chemical potential is referred to as an ideal vapor phase of Se atoms. This explains the large values of the chemical potential at which adsorption takes place, typically around -2.50 eV/atom. The adsorption isotherm is obtained by taking the ensemble average of the number of adsorbed Se atoms at different values of μ and keeping T constant. Periodic boundary conditions are used for the simulation, and boxes containing from 1 to 12 silicalite unit cells have been used. The unit cell size is $20.07 \times 19.92 \times 13.42$ Å³, leading to a 12 unit cells box of $40.14 \times 39.84 \times 40.26$ Å³.

Figure 2 presents adsorption isotherms calculated at $k_B T = 0.04, 0.08, 0.10,$ and 0.12 eV (roughly 473, 923, 1173, and 1393 K). The adsorbed quantity is plotted as a function of the dimensionless ratio $\alpha = \frac{\mu}{k_B T}$. The maximum adsorbed amount is about 45 Se atoms per silicalite unit cell at 473 K and decreases to 40 atoms/unit cell at 1393 K. Calculations at 473 K were performed on three different box sizes (1, 3, and 12 unit cells of silicalite). At 473 K the adsorption branch (Fig. 3) exhibits substeps that depend on the size of the simulation box and on the starting configuration. Starting from a Se₂ dimer located at random in the porous structure, a substep or a shoulder appears for chemical potential values between -2.30 and -2.05 eV/atom. The corresponding adsorbed quantity per unit cell decreases with the simulation box size. On the 12 unit cells box, different starting configurations (Se₂ dimer, Se₄ and Se₆ cyclic molecules located at the channels intersections) were tested. The substep observed starting

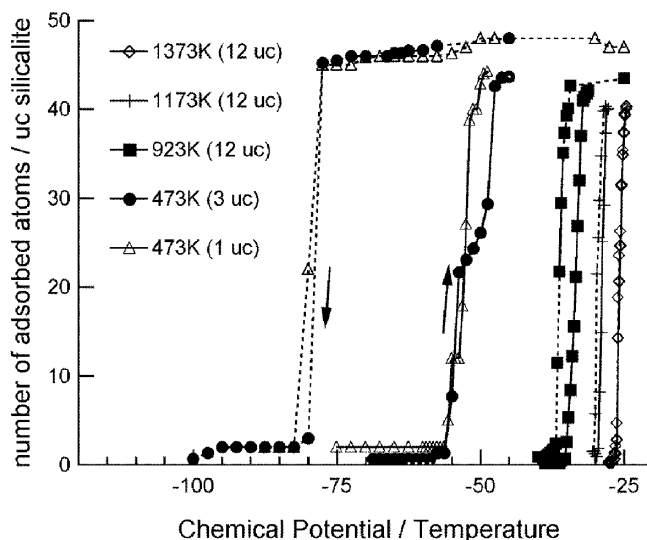


FIG. 2. Adsorption isotherms calculated at four different temperatures for boxes containing 1 to 12 silicalite unit cells. Owing to the very long equilibration times, the desorption branch has not been calculated at 473 K on the largest system. Full curves correspond to adsorption, and dashed curves to desorption.

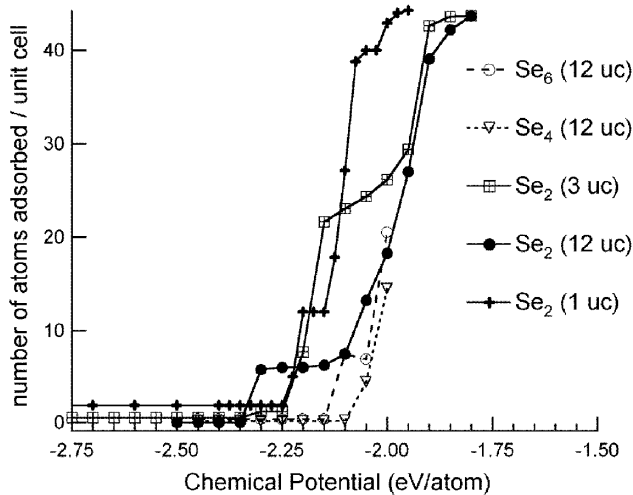


FIG. 3. Adsorption branch calculated at 473 K for different starting configurations (Se_2 , Se_4 , and Se_6 molecules) and different box sizes (1 and 12 unit cells).

from a Se_2 dimer disappears with the other initial configurations. These substeps correspond to the formation of looped chain structures with an average number of Se^I defects below 0.5. The adsorption mechanism can then be interpreted in the following way. At low temperature, cyclic molecules or closed looped chains are more stable than open chains because of the dangling bonds (Se^I defects) present at the ends of open structures. Starting from a Se_2 nucleus, a chain begins to grow for chemical potential values above -2.30 eV/atom. As the simulation boxes are relatively small, both ends meet forming a closed chain that is stable in a chemical potential range up to -2.05 eV/atom. At this stage, the chemical potential (or equivalently the pressure) is large enough to allow branching of chains by Se^{III} defects from which new chains can grow and the zeolite porosity very rapidly fills.

More interesting is the overall shape of adsorption/desorption isotherms. They present a large hysteresis loop the width of which decreases with increasing temperatures and the position of which is shifted towards larger values of α , corresponding to higher pressures. The calculations at 1393 K, which do not correspond to any real situation because silicalite is not stable at such a high temperature, show that the hysteresis loop disappears at high temperature. We can estimate the temperature at which the hysteresis disappears to be of the order of 1300 ± 100 K.

The microscopic adsorption mechanism that proceeds by nucleation and growth of chain structures, the shape of the adsorption isotherms exhibiting large hysteresis loops with a width decreasing with increasing temperatures and a very steep, if not vertical, jump between a low density and a high density phase are characteristic features of a first order phase transition. This behavior is somewhat similar to that observed for capillary condensation of molecular fluids in mesopores [20]. Obviously, in the small channels of silicalite, no capillary transition can occur and the mechanism

of Se adsorption corresponds, in fact, to the condensation of a “gaseous” phase of small molecules or chains of finite length. The temperature at which the hysteresis disappears is the critical temperature of the confined phase of Se, some 500 K below the bulk critical temperature of our model fluid Se. This is very unusual since it is generally stated in the literature [21] that microporous solids such as zeolites (with cavities or channels of few adsorbate diameter in size) are characterized by reversible adsorption (type-I curve in the IUPAC classification). The physical origin of this unusual behavior is easily understood bearing in mind three essential features. First, the porous structure of the silicalite is a three-dimensional one, although the diameter of the channels is very small. Hence a thermodynamic behavior corresponding to a 3D system cannot be ruled out. A second point to consider is the order of magnitude of the Se-Se interaction that is 1 order of magnitude larger than the Se-silicalite interaction. The corrugation of the Se-silicalite interaction energy surface is then expected to play a minor if any role in the adsorption process apart from confining the chains inside the porous structure. The last and probably essential point that explains this first order transition behavior is the preference of Se to form chains or rings that are twofold coordinated structures.

In order to validate this idea, it is interesting to consider a simplified lattice gas-type model. It consists of a series of one-dimensional straight and zigzag channels connected with the same topology as silicalite. The sites are either twofold coordinated (in the channels) or fourfold coordinated (at the intersections). The total energy (E) is taken as a sum of site energies, the energy on each site depending on the number (j) of occupied nearest neighbor sites:

$$E = \sum_{\text{sites } i} E_i(j).$$

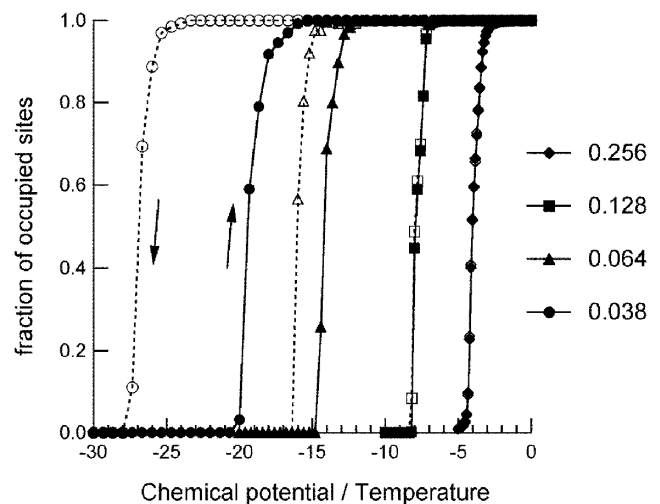


FIG. 4. Adsorption/desorption isotherms calculated on the lattice model with the chain-favoring energy model at four reduced temperatures. Full symbols and lines: adsorption. Open symbols and dashed lines: desorption.

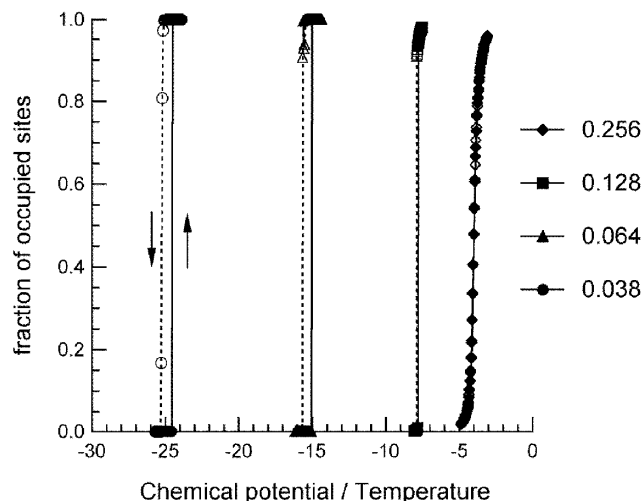


FIG. 5. Adsorption/desorption isotherms calculated on the lattice model with the pairwise additive energy model at four reduced temperatures. Full symbols and lines: adsorption. Open symbols and dashed lines: desorption.

To define the model we simply have to fix the values of E_1 , E_2 , and E_4 . If we take $E_4 = 2E_2 = 4E_1$, the energy is pairwise additive, and we retrieve an Ising-like model. But we can also choose the parameters in order to favor a coordination 2 and consequently chain structures. For example, we can take $E_1 = -1$, $E_2 = -4$, and $E_4 = -3$. The adsorption isotherms calculated at different temperatures for the two energy models are presented on Figs. 4 and 5. The temperatures are rescaled by the energy per site of the completely filled system in order to make things comparable. Although a small hysteresis loop is present at very low temperature, we can see that the pairwise additive model yields classical type-I adsorption isotherms, whereas the chain-favoring energy model yields adsorption isotherms that display the same characteristics as those of Fig. 2. This very simple model proves that the brutal jumps on the adsorption isotherm and the large hysteresis at low temperature that are characteristic of a first order transition are the consequence of the interplay between the three-dimensional topology of the microporous network and the chain favoring energy model.

The calculations presented here give a strong evidence that a first order transition may occur even in a microporous system, when appropriate conditions (3D-microporous network and dominant “lateral” interactions favoring the growth of chains) are encountered. The only limitation of the present calculations comes from the Monte Carlo procedure itself, as it takes no account of

pore blocking or kinetic effects. Although no experiments have been reported up to now, because measuring adsorption isotherms under such conditions is a difficult task, such a measurement would be of fundamental interest, besides the technological interest of nanostructured phases of Se obtained by confinement.

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