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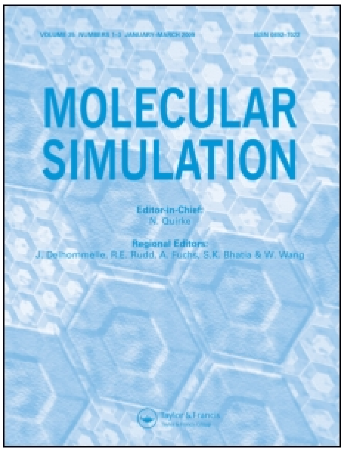

## Molecular Simulation

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# Chain versus Ring Structures of Selenium Confined in $AlPO_4$-5 Zeolite

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**A tight binding grand canonical Monte Carlo simulation of the adsorption of selenium in $AlPO_4$-5 zeolite is presented. We show that the structure of confined Se varies from a stretched chain to a piling of $Se_5$ rings, with intermediate structures combining chains and rings. It depends on the thermodynamic conditions of the adsorption: the ring structures are favored at low temperatures and high pressures; chains are favored at higher temperatures and lower pressures. These results are in qualitative agreement with recent experimental results.**

*Keywords*: Tight binding grand canonical Monte Carlo simulation; $AlPO_4$-5; Zeolites; TRAZ model

## INTRODUCTION

Zeolites play a central role in heterogeneous catalysis and gas separation industrial processes. They are porous crystals offering cages or channels of different shapes and sizes that can be used to displace chemical reaction equilibria and/or control mixture selectivity [1]. Another possibility to benefit from the well-organized zeolitic porous structure is to incorporate metallic or semiconducting elements and use the porosity as a chemical nanoreactor in order to produce nanoclusters, nanowires and tubes. The porous structure enables studying low dimensional confined phases that can become, after matrix removal (using acid leaching for instance), a heterogeneous material with interesting properties. Along these ideas, a series of papers recently dealt with the incorporation of selenium into different zeolites [2–6]. Among them, studies focusing on neutral zeolites are of particular interest since, the adsorbed species interact only weakly with the matrix and the electronic structure of the guest can reasonably be assumed to be unaffected by the neighboring host atoms.

In this paper we study the structure of selenium incorporated into $AlPO_4$-5, a zeolite exhibiting a network of parallel channels of about 7.3 Å diameter. By means of Raman scattering experiments, Poborchii *et al.* [2] evidenced a "torsional melting" transition that corresponds to the release of the dihedral angle rigidity of the selenium chains that are assumed to occupy the channels. Recently, on the basis of X-ray scattering combined with polarized Raman and polarized absorption measurements, Li *et al.* [7] suggested that the structure of the adsorbed phase was a mixture of chains and rings. In order to gain an insight on this problem by means of computer simulations, we performed a series of grand canonical Monte Carlo simulations based on a tight binding model (TB-GCMC) for the selenium–selenium interactions. The confining potential resulting from the supposedly weak Se—Al, Se—O and Se—P interactions is expressed in the framework of the quantum mechanical perturbation theory using the PN-TrAZ model [8,9]. Using the same approach, we showed [10] that the sorption of selenium in silicalite (the siliceous form of ZSM-5 zeolite) proceeds through a first order transition characterized by sharp jumps on the adsorption/desorption isotherms, large hysteresis at low temperature that gradually shrinks with increasing temperature up to a pseudo-critical point around 1300 K. This behavior, unusual for adsorption in

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microporous systems, can be explained considering two essential features:

(i) the ability of selenium to form chains that can be branched or disrupted at a relatively low energy cost and
(ii) the 3-dimensional connected structure of the micro porous network.

Since $AlPO_4$-5 has a much simpler porous structure, a more simple behavior of the adsorption might be expected. The preliminary results presented here show that the adsorption mechanism into pores that are slightly larger than those of silicalite remains non-trivial, driven by a competition between ring and chain structures.

## TOTAL ENERGY MODEL

The interaction of selenium with Al, P and O atoms forming the zeolite structure is assumed to remain weak, in the physiosorption energy range. In this work, we have used a TrAZ form of the original PN-type potential function as reported for adsorption of rare gases and nitrogen in silicalite-1 [7]. The PN-TrAZ potential function is based on the usual partition of the adsorption intermolecular energy restricted to two body terms only [11]: it includes a dispersion interaction term, a repulsive short range contribution and an induction term. Three body dispersion (XYY) terms (where, $X$ is the adsorbate and Y an adsorbent species) can be obtained in principle from the same approach [8] but are neglected in the present study due to the large contrast between the Se—Se and the Se–zeolite interactions. In the TrAZ model, the adsorbate-surface energy ($u_i$) of a selenium gas atom at position $i$ in the simulation box, is given by

$$u_i = \sum_{j\in\{\mathrm{O,Si,H}\}} \left[ A_{ij}\, e^{-b_{ij}r_{ij}} - \sum_{n=3}^{5} f_{2n} \frac{C_{2n,ij}}{r_{ij}^{2n}} \right] - \frac{1}{2}\alpha E_i^2 \quad (1)$$

The sum runs over all atomic sites in the matrix that are oxygen, phosphorus and aluminium atoms. The first term in the sum is a Born–Mayer term representing a two-body form of the short range repulsive energy due to finite compressibility of electron clouds when approaching the adsorbate at very short distance of the pore surface [12]. There is one such term per pair of interacting species. The repulsive parameters ($A_{ij}$ and $b_{ij}$) are obtained from mixing rules of like-atom pairs. The second term in the above equation is a multipolar expansion series of the dispersion interaction in the spirit of the quantum mechanical perturbation theory applied to intermolecular forces [13]. It has been shown that two (and three body) dispersion $C_{2n}$ coefficients for isolated or in-condensed phase species can be obtained from the knowledge of the dipole polarizability and the effective number of polarizable electrons $N_{\mathrm{eff}}$ of all interacting species [7,8] which are closely related to partial charges that can be obtained from *ab initio* calculations. The $f_{2n}$ terms in the above equation are damping functions of the form:

$$f_{2n} = 1 - \sum_{k=0}^{2n} \left[ \frac{(b^{ij} r_{ij})^k}{k!} \right] .e^{-b_{ij}r_{ij}} \quad (2)$$

The role of these damping functions is to avoid divergence of the dispersion interaction at short distance where, the wave functions of the two species overlap (i.e. when the interacting species are at contact) [14]. From a mathematical point of view, the damping functions vary steeply between 0 and unity as the distance between interacting bodies increases. From a physical point of view, the damping functions take into account the possible electronic exchange which has a non-zero probability at short distance even for two close shell structures; for each pair of interacting species, it is parameterized with the $b_{ij}$ repulsive parameter. The damped dispersion multipolar expansion can be seen as a convenient way to make the perturbation theory valid at short inter-atomic separations. The last term in Eq. (1) is the induction interaction as written in the context of the quantum mechanical perturbation theory applied to intermolecular forces [13]. It represents an attractive energy arising from the coupling of the polarizable electronic cloud of the adsorbate of polarizability $\alpha$ at position $i$ with the electric field $E_i$ induced by the charges carried by framework species (O, Al and P) that result from the bonding process within the matrix itself [15]. In total, one has to parameterize three different adsorbate/adsorbent-species potentials; the parameters are given in Table I. The assumption that bonding between the selenium and the zeolite does not involve chemisorption has been validated in the case

TABLE I Se-$AlPO_4$-5 potential parameters

| | *Se—O* | *Se—Al* | *Se—P* |
|---|---|---|---|
| $C_6$ ($E_h a_0^6$) | 89.33 | 22.91 | 41.55 |
| $C_8$ ($E_h a_0^8$) | 2536.0 | 520.8 | 1132.4 |
| $C_{10}$ $E_h a_0^{10}$) | 65,430 | – | – |
| $A(E_h)$ | 603.80 | 1264.7 | 714.30 |
| $b(a_0)$ | 1.9070 | 2.7742 | 3.0410 |

*Zeolite partial charges*
$q(\mathrm{O}) = -0.78e^-$ $q(\mathrm{Al}) = +1.39e^-$ $q(\mathrm{P}) = +1.77e^-$

*Se properties*
Polarizabilities ($a_0^3$) : Number of polarizable electrons:
$\alpha(\mathrm{Se}) = 24.5$ $N_{\mathrm{eff}} = 5.63$

$1E_h = 27.211$ eV and $1a_0 = 0.529177$ Å.

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of the Se/silicalite system by means of *ab initio* computer simulations [10]. The Se–zeolite interaction energy is typically around $-0.2\,\mathrm{eV/atom}$, that is one order of magnitude weaker than the stronger Se—Se covalent bonds and these two interactions are assumed to be, independent, and treated separately. All needed parameters for the dispersion interaction multipolar development can be found from known properties of interacting species. Repulsive parameters for like-pairs are taken from a previous work on the simulation of methane in AlPO$_4$-5 [14]; since atomic selenium has a van der Waals radius very close to that of krypton (2.0 Å; http://www.periodensystem.info/elemente/selen.htm and krypton.htm), we assumed that two selenium atoms will have the repulsive parameters of the Kr—Kr pair ($A_{\mathrm{Kr-Kr}} = 236.3\,E_h$ and $b_{\mathrm{Kr-Kr}} = 1.689\,a_0$; $1\,E_h = 27.211\,\mathrm{eV}$ and $1\,a_0 = 0.529177\,\mathrm{\AA}$).

The Se—Se interaction is described in a tight binding approximation which is a parameterized version of the Hückel theory. We use a minimal s, p$_x$, p$_y$ and p$_z$ atomic orbital basis set and a Slater Koster parameterization to build the Hamiltonian matrix describing the interaction. To avoid the time consuming diagonalization of this matrix, we use the recursion method to calculate the local density of electronic states on each atom. We restrict the continued fraction expansion at the fourth moment's level which means that only first and second neighbors of each site are taken into account to calculate the band energy term. This approximation is quite crude but captures the quantum nature and the directionality of the bonding. In order to describe the weaker interchain or intermolecular bonds formed in the less dense phases of fluid selenium, a dispersion interaction term acting at distances beyond the tight binding cut off radius is added [8], with suitable damping terms to smoothly switch from one to the other. As usual, a repulsive term prevents the collapse of the matter. The model for Se interaction then takes the general form:

$$E_{\mathrm{tot}} = E_{\mathrm{band}} + E_{V\,\mathrm{dW}} + E_{\mathrm{rep}} \tag{3}$$

$$E_{\mathrm{tot}} = \sum_{\mathrm{sites}\,i}\left(\int_{-\infty}^{E_{\mathrm{f}}} E n_i(E)\,\mathrm{d}E\right) - \sum_{i>j}\frac{C_6}{r_{ij}^6}F_2(r_{ij}) + \sum_{i>j} V_0\left(\frac{1}{r_{ij}}\right)^p F_1(r_{ij}) \tag{4}$$

where, $r_{ij}$ is the interatomic distance between sites $i$ and $j$, $n_i(E)$ is the local density of state on site $i$, $E_{\mathrm{f}}$ is the Fermi level and $C_6$ is the attractive constant of the dispersion term (calculated from the polarizability of Se and a number of polarizable electrons). $F_1(r_{ij})$ and $F_2(r_{ij})$ are damping functions. The values of $V_0$, $p$ and the parameters defining the resonance integrals (not shown here) are given in Ref. [16]. This model was shown to accurately describe the structure of high temperature fluid selenium. The calculated thermodynamic properties (liquid–vapor equilibrium, critical point, etc.) of bulk Se were shown to be consistent with the experimental data in Ref. [17].

## COMPUTER SIMULATION TECHNIQUE

We performed standard GCMC simulations on a box containing 11 orthorhombic unit cells of AlPO$_4$-5 stacked along the pore axis to calculate the adsorption isotherms at three temperatures ($kT = 0.04$, $0.06$ and $0.08\,\mathrm{eV}$, corresponding to 190, 420 and 650°C, respectively). Starting with a Se dimer located in the central channel, we gradually raised the chemical potential and recorded the average number of adsorbed atoms. Since these calculations are long, we only calculated the desorption branch of the isotherm at the highest temperature. The chemical potential of Se is referred to a fictitious monoatomic ideal gas of Se. This explains the large values (between $-3.0$ and $-2.2\,\mathrm{eV/atom}$) of the chemical potential at which the adsorption takes place. As expected in the temperature range of the simulations, these values are only slightly larger than the formation energy of bulk Se ($-2.25\,\mathrm{eV/atom}$), because the contribution of the configurational entropy to the chemical potential is small. Because these temperatures are relatively low compared to the cohesive energy of Se, the equilibration of the simulated samples is difficult and very long runs had to be performed. A minimum of $5 \times 10^5$ Monte Carlo macrosteps was performed, each macrostep consisting of randomly performing 1000 attempted displacements, 10 attempted insertion and 10 attempted removals of a Se atom. The maximum number of Se atoms in the 11 unit cells zeolite channel was 115. At $kT = 0.08\,\mathrm{eV}$, such long runs prove to be very efficient (Fig. 1) but at lower temperatures the convergence is very slow and the position of the step on the adsorption isotherm is somewhat uncertain.

## RESULTS AND DISCUSSION

The adsorption isotherms are presented in Fig. 2. Since we put only one Se$_2$ nucleus in the central channel, the adsorbed quantity refers to one channel over 11 unit cells. It should be divided by $11/2 = 5.5$ to be referred to one unit cell of AlPO$_4$-5. The adsorption branches calculated at 190 and 420°C are very similar; the channels are either empty or full and the transition is sharp. The adsorbed Se phase is a piling of Se$_5$ (sometimes Se$_6$) rings perpendicular to the axis of the channel. When the channel is completely filled it corresponds to 2 Se$_5$ rings per

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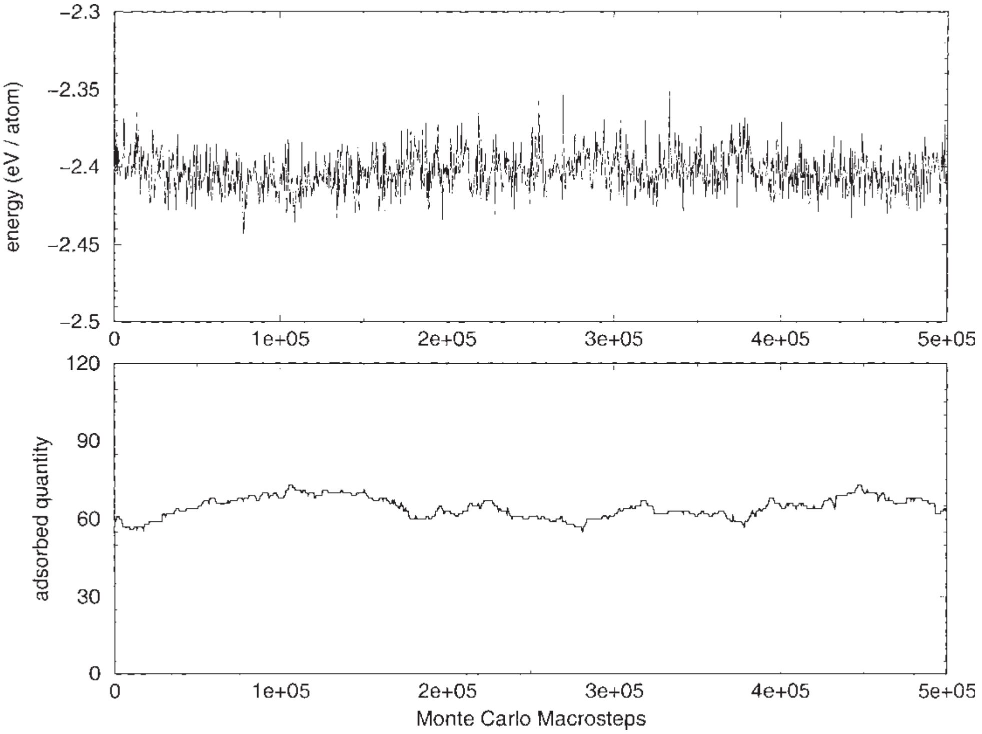

FIGURE 1 Adsorbed quantity (lower panel) and configurational energy (upper panel) as a function of the number of Monte Carlo macrosteps during a GCMC run at $T = 650°C$ ($kT = 0.08\,eV$) and $\mu = -2.92\,eV/atom$.

channel per unit cell, yielding a total number of 20 Se atoms per unit cell of $AlPO_4$-5. The three points at low fillings on the isotherm at 420°C correspond to 1, 2 and 3 rings, respectively. They are probably metastable since there is no obvious reason why such a situation should be stable. It is, therefore, possible that the step on the adsorption isotherm should lie at a lower chemical potential value. The situation is quite different at 650°C; a sharp transition takes place between the nearly empty channel and a half-filled channel (point A in Fig. 2), followed by a gradual, almost reversible, increase of the adsorbed quantity with increasing chemical potential. The structure of the adsorbed phase is a mixture of chains and rings. Figure 3 presents a statistical analysis of the number of atoms belonging to chains or rings. It shows that a gradual chain to rings transition takes place when the adsorbed quantity increases from

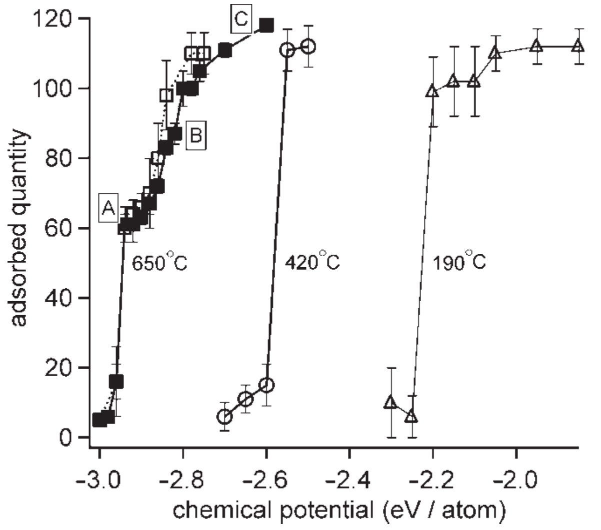

FIGURE 2 Adsorption isotherms calculated at $T = 190$ (triangles), 420 (circles) and 650°C (full squares, adsorption; open squares, desorption). Points A, B and C correspond to the configurations discussed in the text and displayed in Fig. 4.

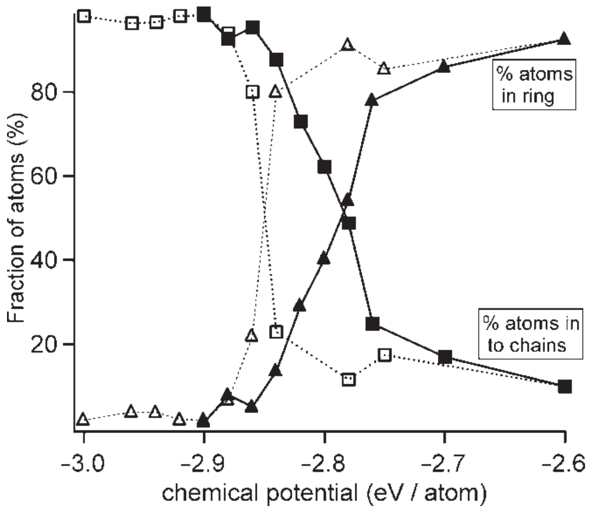

FIGURE 3 Statistical analysis of the fraction of atoms belonging to chains (full squares, adsorption; open squares, desorption) or rings (full triangles, adsorption; open triangles, desorption) as a function of the chemical potential at $T = 650°C$.

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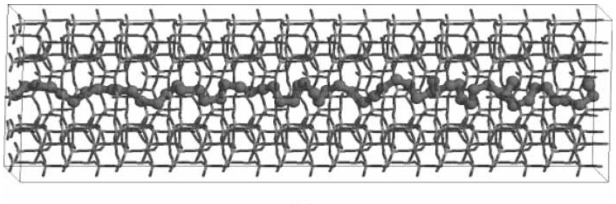
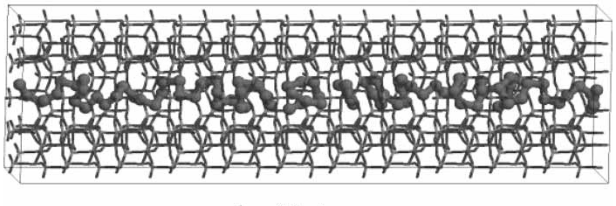
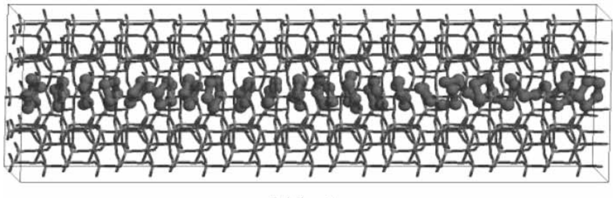


a : 62 atoms



b : 89 atoms



c : 111 atoms

FIGURE 4 Snapshots of three typical configurations obtained at $T = 650°C$. The location of points A, B and C is shown in Fig. 2. (a) 62 Se atoms, chemical potential: $-2.94\,eV/atom$; (b) 89 Se atoms, chemical potential: $-2.82\,eV/atom$; (c) 111 Se atoms, chemical potential: $-2.70\,eV/atom$.

$\sim 60$ to $\sim 118$ atoms. The snapshots of the configurations presented in Fig. 4a–c show that a stretched chain "fills" the channel on point A, that this chain becomes more squeezed (like a compressed spring) up to point B and, due to this compression of the chains, more and more rings (that maximize the filling of the channels) are formed up to point C.

The results of the simulations indicate that the incorporation of selenium into the channels of AlPO$_4$-5 zeolite is indeed more complex than a simple filling of the channels by chains similar to the chains forming the structure of crystalline bulk selenium. At low temperature, a ring structure is clearly favored, not only because it allows a larger number of Se atoms to be adsorbed, but also during the growth of the adsorbed phase. At low temperatures, even at partial filling, Se prefers ring structures. This is the reason why the convergence of the calculations is so difficult. Once a series of rings is formed, the nucleation of another ring close to an existing one is a rare event that proceeds by forming a 3-fold connection from which a piece of chain grows. This chain then splits from the originating ring to form one or several rings that are more stable. We observe a majority of Se$_5$ and occasionally Se$_6$ rings but no larger ring species. This size selectivity depends on the accuracy of the total energy model for Se and of the confining potential. The stability of Se$_5$ compared to Se$_6$ and Se$_8$ isolated molecules is slightly overestimated in our model (formation energies: $-2.31$, $-2.32$, $-2.34\,eV/atom$, respectively) as compared to the experimental ones ($-2.14$, $-2.19$, $-2.24\,eV/atom$, respectively [18]). The main weakness of the selenium/zeolite potential concerns the repulsive term that is obtained empirically through a combining rule given by Böhm and Alhrich [14] and using the fact that selenium is of the same size as Krypton. It is clear at this stage that periodic *ab initio* calculations at a Hartree-Fock level of approximation can provide a better approach to Se—AlPO$_4$-5 repulsive interactions [19].

The stability of chain structures at high temperature and relatively low chemical potential is a consequence of the larger vibrational entropy of the chains and the gradual transition to a ring structure results from the larger number of Se atoms that can be packed when the chemical potential is increased. We may assume that a ring to chain transition with increasing temperature (polymerization of Se rings) should proceed with increasing temperature, but we did not observe it directly upon heating a ring structure or cooling a chain structure.

## CONCLUSION

The GCMC calculations presented here show that the structure of Se incorporated into AlPO$_4$-5 zeolite is not a simple one, ranging from a pure stretched chain structure to a piling of Se$_5$ rings, with intermediate structures combining chains and rings. The resulting structures depend very much on the thermodynamic conditions of the adsorption: the ring structures are favored at low temperatures and high pressures; chains are favored at higher temperatures and lower pressures. These results are in qualitative agreement with the experimental findings of Ref. [7]. They suggest that a polymerization transition might occur upon temperature.

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