

# An Atomistic Simulation Study of Carbon Nanostructure Growth in the Porosity of Different Zeolites

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## ABSTRACT

In this work, we present Grand Canonical Monte-Carlo simulation results for the adsorption of carbon vapour in the pores of various zeolites: AlPO<sub>4</sub>-5, silicalite and faujasite (in its siliceous form). The carbon-carbon interactions are described within the frame of a Tight Binding approach (fourth momentum's method) while the carbon-zeolite interactions are modelled using a PN-TrAZ physisorption potential. In the case of AlPO<sub>4</sub>-5, we demonstrate the possibility of producing ultra small single wall carbon nanotubes (0.4 nm in diameter) in agreement with recent experiments [Wang N., Tang Z. K., Li G.D., J.S. Li, 'Single-walled 4 Å nanotube arrays', *Nature*, 408, 50-51 (2000)]. By contrast, the adsorption of carbon in the porosity of silicalite zeolite just allows the formation of a mesh of intercrossing carbon chains. Siliceous faujasite allows obtaining a 3D connected porous material. The intrinsic stability of such carbon nanostructures was also investigated after removal of the inorganic phase.

**Keywords:** adsorption, Grand Canonical Monte-Carlo simulation, carbon nanotubes

## 1. INTRODUCTION

Zeolites are now involved in the process of manufacturing metallic or semi-conductor nanostructures (clusters, nanowires and nanotubes). The basic idea is the deposition of an element from a vapour or a liquid phase inside the porosity of such crystalline materials that have a narrow pore size distribution. Then, a collection of nanostructures of the deposited element can be obtained after matrix removal (using acid leaching for instance). It is hoped that these nanostructured phases will have a small size dispersion and will be interesting candidates to study low dimension physics. Experimental results for carbon adsorption in zeolites can be found in a series of papers; see for instance reference [1] in which Wang *et al* describe a route to ultra-small Single Wall Carbon Nanotubes (SWNTs) using the porosity of zeolite AlPO<sub>4</sub>-5 made of parallel channels of 7.3 Å in diameter. Another example is the case of selenium adsorption in zeolite silicalite [2]. This purely siliceous zeolite possesses two types of intercrossing channels of 5.5 Å in diameter. Selenium adsorption was

also attempted in the porosity of faujasite [3]; a zeolite that has a porous network made of cages of 10 Å in diameter connected to each other through 7 Å large windows. In this paper, we present the results of a series of Grand Canonical Monte Carlo simulations of carbon adsorption in the porosity of these three zeolite frameworks: AlPO<sub>4</sub>-5, silicalite and (siliceous) faujasite.

## 2. COMPUTATIONAL METHODS

### 2.1. The adsorbate-zeolite potential energy

The interaction of carbon with Si, Al, P and O atoms participating to the different zeolite frameworks considered in this work, is assumed to remain weak, in the physisorption energy range. This is the reason why we have used a PN-TrAZ potential function as originally reported for adsorption of rare gases and nitrogen in silicalite-1 [4]. The PN-TrAZ potential function is based on the usual partition of the adsorption intermolecular energy restricted to two body terms only. In the TrAZ model, the interaction energy ( $u_i$ ) of a (neutral) carbon atom at position  $i$  with the zeolite framework species, is given by:

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

The sum runs over all atomic sites in the matrix that are oxygen, phosphorus and aluminium atoms for AlPO<sub>4</sub>-5 and oxygen and silicon for silicalite and faujasite in its siliceous form. 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. There is one such a term per pair of interacting species. The repulsive parameters ( $A_{ij}$  and  $b_{ij}$ ) are obtained from mixing rules of like-atoms pairs (see below). 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. 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  $N_{eff}$  of all interacting species [5], 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:

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

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). The last term in equation (1) is the induction interaction as written in the context of the quantum mechanical perturbation theory applied to intermolecular forces [6]. 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, Si and P) that result from the bonding process within the matrix itself. In total, one has to parametrize four different adsorbate/adsorbent-species potentials; all parameters are given in Table 1. The repulsive interaction parameters for the C-C pair are taken from previous works on adsorption of xylene in faujasite zeolite [7] and methane in AlPO<sub>4</sub>-5 [8]. They are subsequently combined to those of the zeolite species [4].

## 2.2. The adsorbate-adsorbate interaction through a total energy model

The adsorbate-adsorbate (C-C) interactions are described in a tight binding approximation (TB) that 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 carbon-carbon 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 neighbours 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 bonding in carbon compounds (from  $sp$  to  $sp^3$  hybridization). As usual in the TB formalism (or in the Hückel theory for chemical bonding), a repulsive term prevents the unphysical collapse of matter. The model for C-C interactions then takes the general form:

$$E_{tot} = E_{band} + E_{rep} + E_{disp} \quad (3)$$

$$E_{tot} = \sum_i \int_{-\infty}^{E_f} E n_i(E) dE + \sum_{j>i} V_0 \left( \frac{1}{r_{ij}} \right)^p F_l(r_{ij}) \quad (4)$$

where  $r_{ij}$  is the interatomic distance between sites  $i$  and  $j$ ,  $n_i(E)$  is the local density of state on site  $i$ ,  $E_f$  is the Fermi level.  $F_l(r_{ij})$  is a damping function. The tight binding repulsive potential parameters were adjusted on known solid carbon phases and will be given in a separate publication [9].

	C-Si	C-O	C-Al	C-P
$C_6 (E_h a_0^6)$	13.156	36.580	9.3780	17.032
$C_8 (E_h a_0^8)$	257.280	834.82	162.44	371.76
$C_{10} (E_h a_0^{10})$	—	20100	—	—
$A (E_h)$	468.952	234.68	491.89	277.57
$b (a_0)$	1.975	1.9440	2.8650	3.1340
<b>C properties</b>				
<i>Polarizability</i> $C (a_0^3)$	<i>Number of polarizable</i>			
9.80	electrons: $N_{eff} = 2.65$			
<b>Zeolite partial charges</b>				
<i>AlPO<sub>4</sub>-5: <math>q(O) = -0.78 \bar{e}</math>, <math>q(Al) = +1.39 \bar{e}</math>, <math>q(P) = +1.77 \bar{e}</math></i>				
<i>Silicalite: <math>q(Si) = 2 \bar{e}</math>, <math>q(O) = -1 \bar{e}</math></i>				

Table 1: C-Silicalite, C-AlPO<sub>4</sub>-5 and C-faujasite potential parameters. [1  $E_h = 27.211$  eV and 1  $a_0 = 0.529177$  Å]

## 2.3. Simulation technique

We performed standard Grand Canonical Monte Carlo (GCMC) simulations [10] on a periodic box containing a number of zeolite unit cells. For instance, we have considered 5 orthorhombic unit cells of AlPO<sub>4</sub>-5 stacked along the pore axis. Starting with a C<sub>2</sub> dimer, we gradually raised the chemical potential and recorded the average number of adsorbed carbon atoms. This allowed us to calculate carbon adsorption isotherms. Note that the chemical potential of the carbon atoms is referred to that of a fictitious monoatomic ideal gas. This explains the large values of the chemical potential at which the adsorption takes place (see below): between  $-5.5$  and  $-6$  eV/atom. As expected considering the temperature range of the simulations, these values are only slightly larger than the carbon-carbon bonding energy ( $-6.98$  eV); the contribution of the configurational entropy to the chemical potential being rather small. A minimum of  $5 \cdot 10^5$  Monte Carlo macro-steps was performed, each macro-step consisting of randomly performing 1000 attempted displacements, 10 attempted insertion and 10 attempted removals of an adsorbate atom. In order to accelerate GCMC simulation runs, we calculated the adsorbate/substrate interaction using

an energy grid, which splits the simulation box volume into a collection of voxells. The adsorbate/substrate potential energy was calculated at each corner of each elementary cube (about  $0.2^3 \text{ \AA}^3$ ). The adsorbate/substrate energy is then obtained by an interpolation procedure of the 3D energy grid. This procedure allows simulating adsorption with no direct summation over the matrix species in GCMC runs and is computationally very efficient [10]. Note that we used the symmetry elements of the different zeolite unit cell to reduce the size of the carbon-zeolite energy grid. Our simulation method clearly mimics the experimental carbon vapour deposition method (CVD) that is used to produce carbon nanostructures from zeolites.

### 3. RESULTS AND DISCUSSION

#### 3.1. $\text{AlPO}_4\text{-5}$

An adsorption isotherm of carbon at 1000 K in  $\text{AlPO}_4\text{-5}$  is shown in Figure 1. The carbon growth begins with a helical chain composed of 48 atoms that gradually includes loops and transforms in a defective Single Wall Nano-Tube (SWNT) with a diameter of  $\sim 4 \text{ \AA}$  in agreement with recent experimental results [1]. It is composed of five, six and seven member rings. The different steps that we observed during the growth of this ultra small SWNT are illustrated in Figures 2a, 2b and 2c. The final tubular structure was thermalized at 2000 K in order to cure defects. The bond angle and neighbours distributions indeed show a decrease of the number of defects during this graphitisation process. We have further tested the effects on the chemical potential increment and shown that low pressure and temperature conditions are needed to obtain the more stable structures during the CVD process. The typical carbon-zeolite interaction energy is around  $-0.1 \text{ eV}$ , *i.e.* much smaller than that of the C-C bonding energy and characteristic of a physisorption as expected.

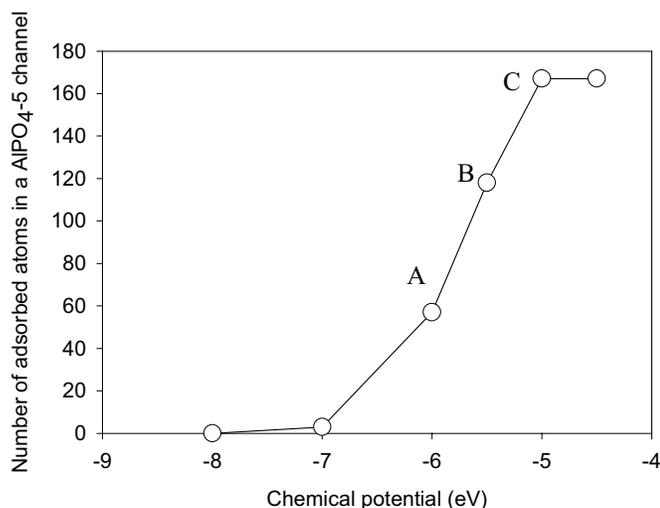


Figure 1. C adsorption isotherm at 1000 K in  $\text{AlPO}_4\text{-5}$

Fig. 2a

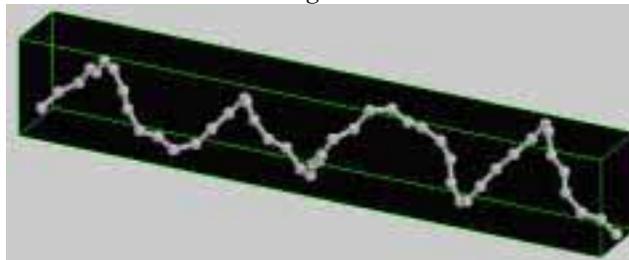


Fig. 2b

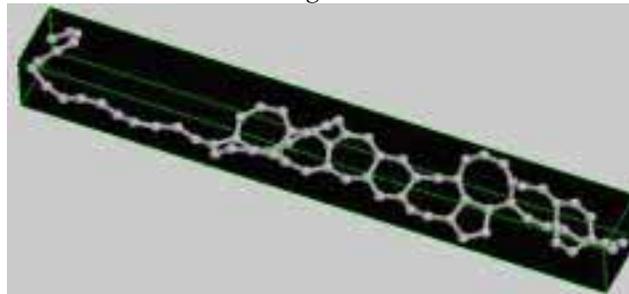


Fig. 2c

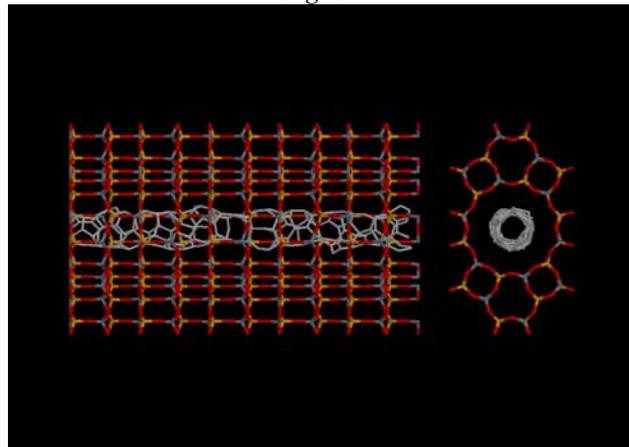


Figure 2. Equilibrium configurations for carbon adsorption at points A (fig. 2a), B (fig. 2b), C (fig. 2c) on Figure 1.

Note that recent *ab initio* calculations [11] of perfect SWNTs in  $\text{AlPO}_4\text{-5}$  shows that there is no chemical bonding process occurring between the carbon nanostructure and the inorganic phase. This fully justifies our choice for the carbon-zeolite potential model. A subsequent relaxation of our in-cavity-obtained carbon nanotube is performed by setting the matrix-carbon interactions to zero in order to mimic the dissolution of the inorganic phase as done in experiment. It shows the intrinsic stability: the tube did not collapse nor explode. This indicates that such small tube may exist after the removal of the zeolite matrix; this is indeed an important result if this synthesis route is chosen for the production of size controlled ultra-small SWNT's.

### 3.2. Silicalite

In the case of silicalite, we obtained a similar adsorption curve at 1000K. The smallness of the channel diameter did not allow the formation of aromatic carbon nanostructures but a mesh of intercrossing alcene-like chains. This indicates that there is a size limit for the production of aromatic carbon nanostructures.

### 3.3. Faujasite

Carbon adsorption in faujasite at 1000 K leads to the formation of a 3D connected porous carbon structure that is the (negative) replica of the original zeolite cavity network (see figures 3a and 3b). The adsorption isotherm being again very similar to that obtained for AlPO<sub>4</sub>-5. The resulting structure is also stable upon matrix removal and has probably very high mechanical properties. It is interesting to note that this structure is close to those predicted by Terrones *et al* using Schwarz minimal curved

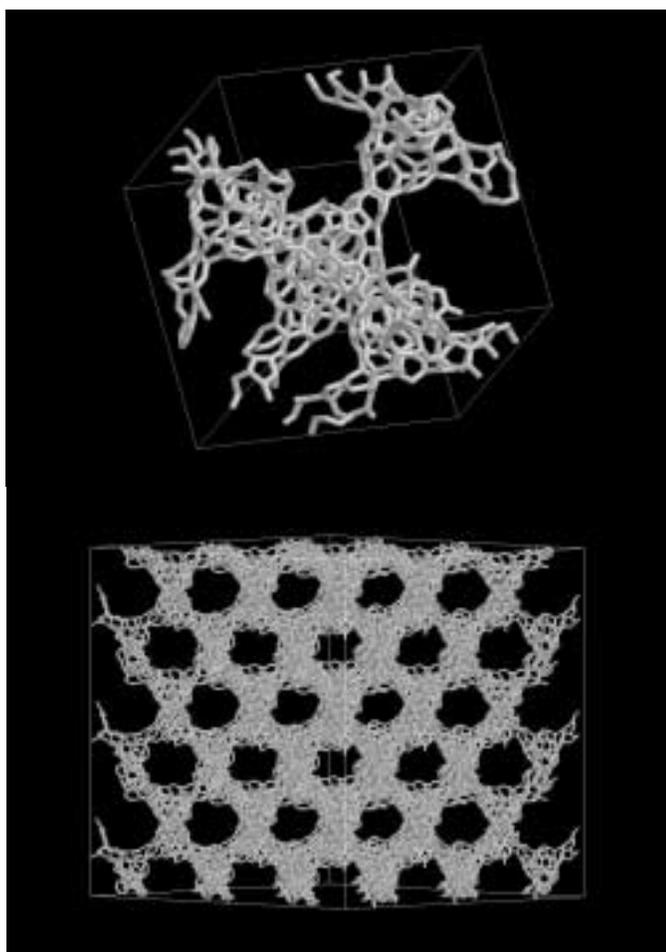


Figure 3. (a) Carbon replica of faujasite zeolite at 1000 K. (b) the same but replicated a 125 times to show the porosity of the carbon replica.

surfaces [12,13]. We are currently calculating adsorption capacity of this faujasite carbonaceous replica for gases such as molecular hydrogen and methane.

## 4. CONCLUSION

We have performed Grand Canonical Monte-Carlo (GCMC) simulations of Chemical Vapour Deposition of carbon in AlPO<sub>4</sub>-5, silicalite and faujasite zeolites based on a tight binding model for the adsorbate-adsorbate interactions that enables to account for covalent bonding along with a realistic model for adsorbate-substrate interactions. The GCMC results show that carbon adsorption in AlPO<sub>4</sub>-5 from an atomic gas phase, allows eventually the formation of an ultra small nanotube of 0.4 nm in diameter, in agreement with experiment. Our simulations show that this tube is stable upon matrix removal. In the case of silicalite, we only obtain a mesh of intercrossing carbon chains but no aromatic carbon structures indicating that the smallest host cavity size for growing aromatic carbon nanostructures is around 7 Å. In the case of zeolite faujasite, we obtain a 3D connected porous carbon structures that is stable upon matrix removal. It is presently considered as a possible gas storage device for methane and hydrogen.

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