

# A Grand Canonical Monte-Carlo Simulation of the textural, Mechanical and Adsorption Properties of Faujasite zeolite carbon replica.

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## ABSTRACT

In this work, we present a Grand Canonical Monte-Carlo simulation results for the adsorption of carbon vapour in the pores of faujasite zeolite (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. 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, for there mechanical properties, and there gas adsorption properties. We also have shown that the replica hydrostatic mechanical properties are much better compared to the zeolite and with a very low density. The comparison of the calculated structure factor with experimental studies has given a criterium to characterize the perfect replica. Therefore, we calculated the pore size distribution (PSD) offering to experiments a precision more.

**Keywords:** adsorption, Grand Canonical Monte-Carlo simulation, carbon, zeolite, faujasite, Y zeolite.

## 1. INTRODUCTION

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. Carbon 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 previous works, we demonstrate the possibility of producing ultra small single wall carbon nanotubes from a AlPO<sub>4</sub>-5 zeolite, with a 0.4 nm 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, we show that the adsorption of carbon in the porosity of silicalite zeolite just allows the formation of a mesh of intercrossing carbon chains. Zeolites are now involved in the process of manufacturing metallic or semi-conductor nanostructures (clusters, nanowires and nanotubes). In this paper, we present some properties of faujasite replica resulting of a series of Grand Canonical Monte Carlo results.

## 2. COMPUTATIONAL METHODS

### 2.1. The adsorbate-zeolite potential energy

First, to calculate the interaction of carbon with Si, Al, P and O atoms participating to the different zeolite frameworks considered in this work, it 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:

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

The sum runs over all atomic sites in the matrix that are oxygen and silicon for 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. 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 and 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 and Si) 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 and 2. 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].

On the other hand, to simulate the adsorption of N<sub>2</sub> in the faujasite replica, we used the standard GCMC method with Lennard-Jones potential functions to describe the N<sub>2</sub>-N<sub>2</sub> and N<sub>2</sub>-C interactions, the cross-parameters being obtained with the usual Lorentz-Berthelot rules. We calculated the N<sub>2</sub> adsorption isotherms at 77. To calculate the saturated pressure P<sub>0</sub> of the LJ fluid at different temperatures, we used the state equation given by Kofke [9]. The same parameters were used to calculate the PSD.

## 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<sub>x</sub>, p<sub>y</sub> and p<sub>z</sub> 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<sup>3</sup> 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:

$$E_{tot} = E_{band} + E_{rep} + E_{disp} \quad (2)$$

$$E_{tot} = \sum_i \int_{-\infty}^{E_f} E n_i(E) dE + \sum_{j>i} V_0 \left( \frac{1}{r_{ij}} \right)^p F_I(r_{ij}) \quad (3)$$

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.  $F_I(r_{ij})$  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 [10].

	C-Si	C-O		
$C_6(E_h a_0^6)$	13.156	36.580		
$C_8(E_h a_0^8)$	257.280	834.82		
$C_{10}(E_h a_0^{10})$	—	20100		
$A(E_h)$	468.952	234.68		
$b(a_0)$	1.975	1.9440		
<hr/>				
C properties				
$Polarizability C(a_0^3)$	<i>Number of polarizable electrons: N<sub>eff</sub> = 2.65</i>			
9.80				
<hr/>				
Zelite partial charges				
AlPO <sub>4</sub> -5: q(O) = -0.78 e, q(Al) = +1.39 e,				
q(P) = +1.77 e				
Faujasite: q(Si) = 2 e, q(O) = -1 e				

Table 1: C-faujasite potential parameters. [1 E<sub>h</sub> = 27.211 eV and 1 a<sub>0</sub> = 0.529177 Å]

	$\sigma$ (Å)	$\epsilon$ (K)
C-N <sub>2</sub>	3.609	100.4
N <sub>2</sub> -N <sub>2</sub>	3.400	28.0

Table 1: Lennard-Jones parameters for the N<sub>2</sub> replica adsorption.

## 2.3. Simulation technique

We performed standard Grand Canonical Monte Carlo (GCMC) simulations [11] on a periodic box containing a number of zeolite unit cells. 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. As expected considering the temperature range of the simulations, these

values are only slightly larger than the carbon-carbon bonding energy (-7.04 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 interactions using an energy grid, which splits the simulation box volume into a collection of voxels. 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 [11]. Our simulation method clearly mimics the experimental carbon vapour deposition method (CVD) that is used to produce carbon nanostructures from zeolites.

### 2.3. The Gelb-Gubbins analysis for pore size distribution:

We determine the geometric properties of the Y-zeolite carbon replica using a Monte Carlo integrations related to those developed for previous stereological studies [12] [13]. This method consists of test points randomly placed in the simulation box, and if an adsorbate particle placed at a test point overlaps with the pore material (that is inside the accessible surface), the point is accumulated. The porosity is just the number of misses divided by the total number of insertions. We use the LJ parameters (used before to calculate  $\text{N}_2$  adsorption isotherms) to determine the accessible surface. This method insures that we calculate the “real porosity” of the nanostructures. In recent works [14], we compared this method applied to our simulation with the model following the implementation of Tarazona’s [15] Non Local DFT (NLDFT) described by Lastoskie et al. [16].

## 3. RESULTS AND DISCUSSION

### 3.1. Structures properties

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 figure 1a). The resulting structure is also stable upon matrix removal (see figure 1b) and has probably very high mechanical properties compared to her density. It is interesting to note that this structure is close to those predicted by Terrones *et al* using Schwarz minimal curved surfaces [17,18]. We calculated the structure factor obtained from the atoms coordinates, and using periodic condition boundaries (see figure 2). We confirm that the

replica, the pristine and the heated, is conserving the strong (111) reflection peak of the Y zeolite.

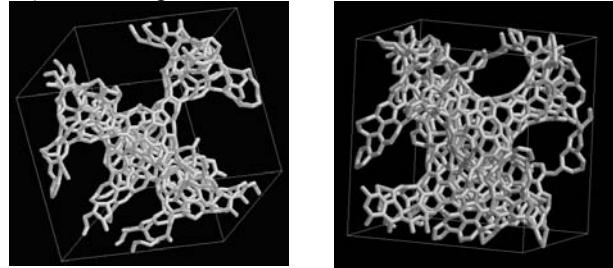


Figure 1. (a) Carbon replica of faujasite zeolite at 1000 K.  
(b) the same but Heated at 3000 K and cooled at 300 K

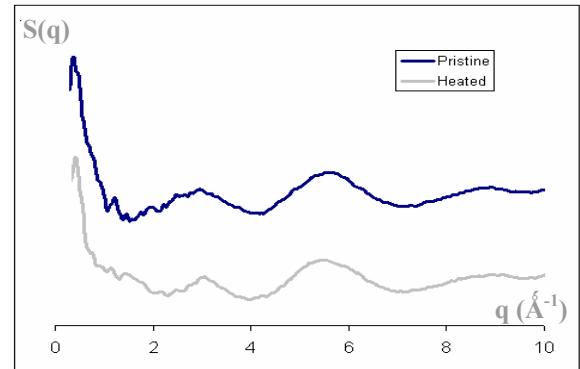


Figure 2. Structure factors of the a) pristine replica at 1000K and for b) the Heated replica and cooled at 300K.

The pristine and relaxed after a heat treatment structures show a spectrum with only one peak corresponding to the unit cell of the zeolite proving that the integrity of the template was conserved. Lee, Han and Hyeon shown experimentally a peak appearing at 23 ( $2 \cdot 0$ ) corresponding to  $1.8 \text{ \AA}^{-1}$ . This peak could be associated to an amorphous region remainder from the experimental method. Moreover, we can see the comparison with an amorphous structure corresponding to a coke of saccharose obtain at 400 K [19] confirming this possibility. Recently, Hou *et al* [20] have shown a new method to obtain replica with after heat treatment, they improved the texture of the replica. We calculated the Bulk modulus of the faujasite using a GULP model [21], which is a core-shell potential, giving the Hessian matrix, and after diagonalization, we obtain a Bulk Modulus of  $B_0=59 \text{ GPa}$ . Thus, the hydrostatic properties of the replica were obtain from the calculation of the energy as a function of the hydrostatic pressure, giving a  $B_0=700 \text{ GPa}$  for a density of  $0.9 \text{ cc/g}$ . Thus, we have simulated the molecular nitrogen adsorption isotherms at 77K, using a Grand Canonical Monte-Carlo method, and with a LJ model. We obtained a good agreement with some results depending of the samples (see figure 3). However, we did not attribute why we obtained an insufficiency in the quantity of gas adsorbed compared to the best replica of Kyotani, unless an increasing of the porosity during the zeolite leaching, or a mesoporosity underestimated in their experiments or even if a resulting part of amorphous carbon is coexisting in their samples.

Therefore, to go into the discussion, we calculated the PSD estimated with the Gelb-Gubbins method (see figure 4).

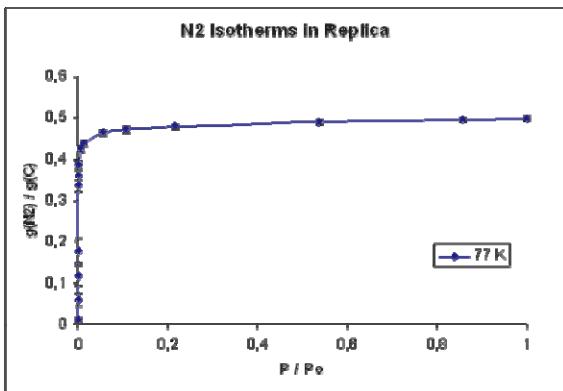


Figure 3. N<sub>2</sub> Isotherm at 77 K. (P<sub>0</sub> = 93211 Pa)

Due to this topological method, we can calculate precisely the PSD of our structures and then compare to the DFT method applied to the N<sub>2</sub> isotherms. First, the differential PSD curve show that our replica is a completely made of spherical pores with a size of 10 Å diameter offering a high microporosity. Besides, we obtained an adsorbed volume around 0.7cc/g, in good agreement with experimental results.

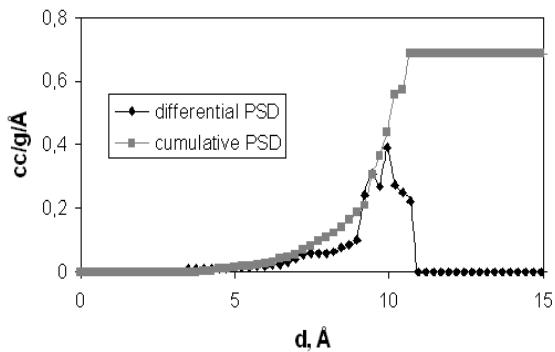


Figure 4. a) Exact differential and cumulative Pore Size Distribution PSD using Gelb-Gubbins model giving the exact PSD of our structure.

#### 4. CONCLUSION

We have performed Grand Canonical Monte-Carlo (GCMC) simulations of Chemical Vapour Deposition of carbon 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. We obtain a 3D interconnected porous carbon structures from the zeolite faujasite, that is stable upon matrix removal. Beside, we characterized the textural structure of this replica, the nitrogen adsorption properties, and his pore size distribution. The hydrostatic mechanical properties of this replica has exhibited a very higher bulk modulus compared

to the faujasite and is really interesting for its very low density. It is presently considered as a possible gas storage device for methane and hydrogen.

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