

Realistic molecular models of porous carbons obtained from Reverse Monte Carlo simulations

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ABSTRACT

In this work we present molecular models of two saccharose based carbons using a Reverse Monte Carlo (RMC) procedure that incorporates an energy penalty term. The resultant molecular models reveal the disordered nature of porous carbons and reproduce the experimental pair correlation functions with good accuracy. The presence of an energy penalty term reduces the probability of having many 3 and 4 member rings, reported in many previous RMC studies on modeling carbons, and also correctly describes the local environment of carbon atoms. Using a ring connectivity method, we also show that the molecular models obtained contain some defective graphene segments which are distorted in a complex way. To further characterize our models we calculated the adsorption isotherms of argon at 77.4 K in the resultant molecular models using Grand Canonical Monte Carlo (GCMC) simulations. The molecular models are further validated by comparing the simulated isosteric heat of adsorption with that obtained from the experiments.

INTRODUCTION

Porous carbons are disordered materials with heterogeneous pore structures. These materials have found widespread application in industry owing to their excellent surface activity [1]. However, the microscopic structure of these materials is still a matter of debate. Thus, suitable atomistic models need to be developed that realistically describe the microstructure of these materials, in order to understand the different properties of these materials, and to help in tailoring them for specific purposes.

In recent times, reconstruction methods have been popular to develop molecular models of amorphous substances. In this approach a 3D structural model is built that is consistent with a set of experimental data. Reverse Monte Carlo (RMC) [2] is one such reconstruction method, in which the molecular model is built to match experimental structure factor data from X-ray or neutron diffraction.

However, RMC is a fitting procedure in which (subject to some constraints) the model is adjusted to best fit $g(r)$ from experiment. The stability of the resultant models cannot be guaranteed, i.e. the resultant models obtained might contain

some unphysical features such as 3 and 4 member rings, which are high energy structures. In a previous work [3] we studied the stability of the models obtained from a constrained RMC procedure [4] for saccharose - based carbons by relaxing them using two different approaches that realistically describe the interaction between the carbon atoms. We found that the local structure of these models change upon relaxation. Moreover, these models contain some 3 and 4 member rings; these are eliminated upon relaxation.

In a more recent work we presented a simulation protocol [5], based on Hybrid Reverse Monte Carlo (HRMC), in which the algorithm attempts to simultaneously minimize the error in the radial distribution function and also the total energy of the system. This is achieved by adding an energy penalty term in the original RMC procedure. The presence of the energy term decreases the probability of having unrealistic structures, while simultaneously matching the experimental data. The use of such an energy term in the acceptance probability of the RMC procedure has been used before by Snook and coworkers [6,7] in the study of amorphous carbons.

We use our simulation protocol [5] to develop molecular models for two porous carbons obtained from saccharose, previously used by Pikunic et al. [4] and named CS400, CS1000. Here 400 and 1000 represent the temperatures at which these materials are carbonized. We develop molecular models by considering carbon and hydrogen atoms and neglect the presence of other hetero atoms. The amount of carbon and hydrogen present in the samples is obtained from the composition data [4]. The carbon-carbon, carbon-hydrogen and hydrogen-hydrogen interactions are modeled using the Reactive Empirical Bond Order (REBO) potential [8].

SIMULATION DETAILS

The Reverse Monte Carlo method was initially proposed by McGreevy and Pustzai [2]. The idea is to generate an atomic configuration of a system that matches the structural properties of the real system obtained by experiment. Throughout the simulation the differences between the simulation and experimental structural properties are minimized. The most commonly used structural property in

RMC methods is the structure factor, $S(q)$ and the quantity to be minimized is

$$\chi^2 = \sum_{i=1}^{n_{\text{exp}}} [S_{\text{sim}}(q_i) - S_{\text{exp}}(q_i)]^2 \quad (1)$$

where S_{sim} is the structure factor for the model material and S_{exp} is the experimental structure factor. After determining S_{sim} for a given atomic configuration, atoms are moved randomly in a Monte Carlo procedure to obtain a new configuration. The probability of acceptance of a new atomic configuration is given by

$$P_{\text{acc}} = \min \left[1, \exp \left\{ -\frac{1}{T_{\chi}} (\chi_{\text{new}}^2 - \chi_{\text{old}}^2) \right\} \right] \quad (2)$$

where T_{χ} is a weighting parameter.

In our simulation protocol we introduce an energy penalty term in the acceptance criteria. The energy of the system is calculated using the REBO potential of Brenner [8], which is based on Tersoff's covalent bonding formalism [9],

$$U_{ij} = V_{ij}^R(r_{ij}) + b_{ij} V_{ij}^A(r_{ij}) \quad (3)$$

It has a pair repulsive, V_{ij}^R , a pair attractive, V_{ij}^A , potential term and a bond order term, b_{ij} , which weights the attractive part of the potential with respect to the repulsive part. The bond order term is a many body term, which depends on the local environment of atoms i and j . A variety of chemical effects that affect the strength of the covalent bonding interaction are all accounted for in this term. Coordination numbers, bond angles and conjugation effects all contribute to the strength of a particular bonding interaction in the REBO potential. The REBO potential is a short ranged potential and does not contain any dispersion interactions. The probability of acceptance of the new atomic configuration is given by:

$$P_{\text{acc}} = \min \left[1, \exp \left(-\frac{1}{T_{\chi}} \left((\chi_{\text{new}}^2 - \chi_{\text{old}}^2) + \frac{1}{w} (U_{\text{new}} - U_{\text{old}}) \right) \right) \right] \quad (4)$$

where U_{new} and U_{old} are the energies of the new and old configurations respectively, and w is a weighting parameter used to weight the energy term with respect to the structure one.

RESULTS

We used our simulation protocol to build molecular models for CS400 and CS1000 in a 25 angstrom box. The density of CS400 and CS1000 are 1.275 g/ml and 1.584 g/ml respectively as obtained from Hg porosimetry [4]. In figures

1 and 2 we show the comparison between the simulated and experimental pair correlation functions. The experimental and simulated pair correlation functions for both the samples are in good agreement. Moreover, it can be seen from figures 1 and 2 that CS1000 has more structure as compared to CS400, as the peaks are more pronounced for CS1000, and it has long range correlations. The bond angle distributions (not shown here) for the two and three fold coordinated carbon atoms are also in agreement with the local coordination of the carbon atoms for both the models. Upon calculating the ring statistics (not shown here) we found that CS400 does not contain any of 3 and 4 member rings and CS1000 has a 3 member ring. However, previous RMC studies on carbon have reported a large population of these small rings [6,10]. These small rings are high energy structures and are thus unphysical.

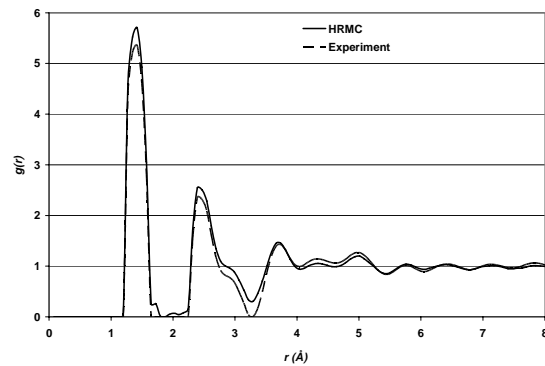


Figure 1. Pair correlation function of CS400 obtained from experiment and from the model.

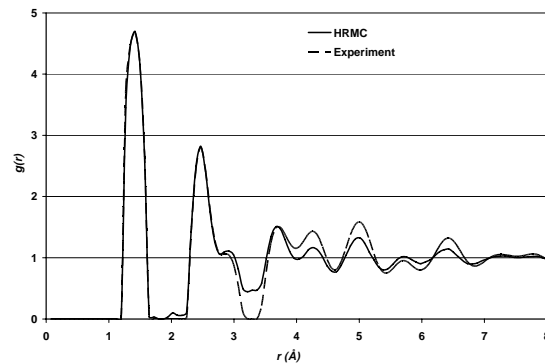


Figure 2. Pair correlation function of CS1000 obtained from experiment and from the model.

In atomistic models of amorphous materials, ring statistics provide a measure of medium range order. However, while ring statistics tell us the number of rings of various sizes present in the model, they do not give us any information about the arrangement of rings, e.g. if the rings are clustered and how big is a cluster. In a recent work [11] we presented a method to calculate the ring connectivity, or clustering of rings. We first calculate the rings present in the model using the shortest path criteria of Franzblau [12], and then find the rings that are connected together and group them into

clusters. We find clusters containing 5-, 6- and 7- carbon member rings in our models. After isolating the clusters, we found that they resemble defective graphene segments twisted in a complex way. In figure 3 we show snapshots of the molecular models obtained using our simulation protocol. The different color codes represent different graphene segments present in the models.

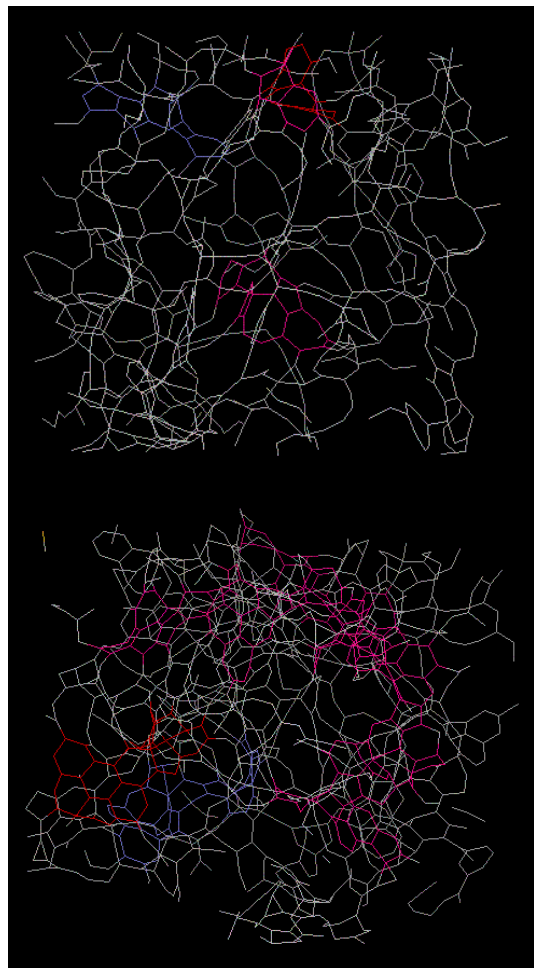


Figure 3. (a) Snapshot of CS400 model obtained from the simulations. The different color code (except grey) represent different graphene segments. (b) the same for CS1000.

Upon analyzing the graphene segments in both the models we found that CS1000 has more graphene segments and the graphene segments are larger as compared to CS400. Apart from the graphene segments there are many carbon atoms which do not belong to any of the graphene segments and are arranged in a chain like fashion. CS400 is mainly composed of carbon atoms arranged in a chain fashion as can be seen from figure 3(a).

To further characterize our models we calculated the geometric pore size distribution (PSD) using the method of Gelb and Gubbins [13]. The PSD (not shown here) reveal that both the carbon models contain micropores with the maximum pore size being 8 angstrom. The porosity was

found to be higher for CS400 as compared to CS1000. We also calculated the argon adsorption at 77.4 K in the resultant models using GCMC simulations. The adsorption isotherms are shown in figure 4 and are typical of microporous solids with micropore filling occurring at a low pressure. The total amount adsorbed is higher for CS400 as compared to CS1000, owing to its high porosity. From figure 4 it can be seen that the micropore filling starts at a lower pressure for CS1000 as compared to CS400. This is due to the comparatively high density of carbon atoms in CS1000 as compared to CS400. Thus an adsorbate molecule in CS1000 feels the presence of a large number of carbon atoms as compared to the adsorbate in CS400.

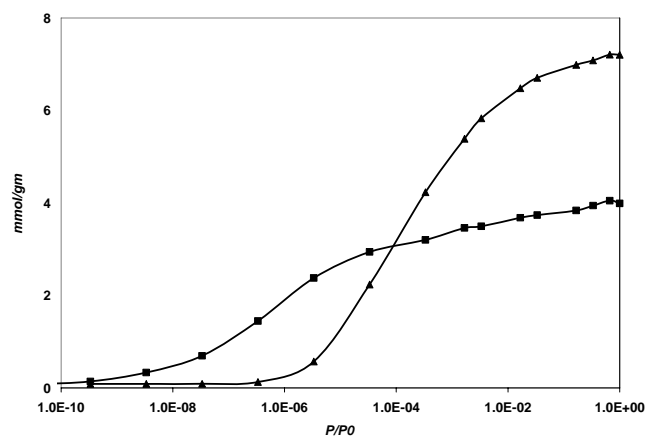


Figure 4. Argon adsorption isotherm at 77.4 K for in CS400 (triangles) and CS1000 (squares) obtained using GCMC simulations.

We also calculated the isosteric heat of adsorption in our models. The fluid-fluid and fluid-wall contribution (not shown here) were also calculated during the simulation. We found that the fluid-wall contribution dominates for both the samples at all the pressures. To validate our models we compared the simulated and experimental isosteric heat of adsorption and is shown in figures 5 and 6. The experimental and simulated isosteric heat of adsorption are in good qualitative agreement for both the carbon samples. The low coverage heat is reproduced well for CS400, but less well for CS1000. However, the overall agreement is good for CS1000. The simulated and experimental values differ at high loading for CS400. In a previous work Pikunic et al. developed molecular models of CS400 and CS1000 in a 50 angstrom box using a Constrained Reverse Monte Carlo procedure [4]. They also calculated the isosteric heat of adsorption of argon in their resultant models and obtained quantitative agreement with experiments [14].

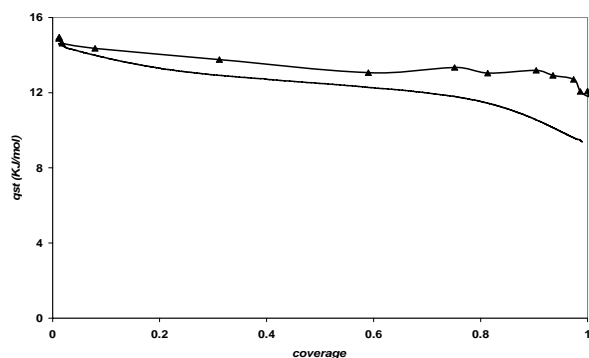


Figure 5. Isosteric heat of adsorption of argon at 77.4 K for CS400. Shown are experiment (solid line) and simulation in (triangles).

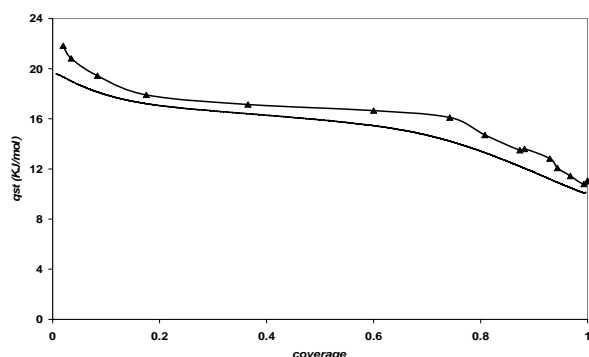


Figure 6. As for Figure 5, but for CS1000.

CONCLUSIONS

We have developed molecular models for 2 saccharose based carbons using a RMC method that incorporates an energy penalty term. The resultant models, as seen from the snapshots, reveal the disordered nature of porous carbons and have complicated pore geometry. The resultant molecular models reproduce the experimental pair correlation functions with good accuracy. The presence of the energy term in the acceptance criteria penalizes the formation of unphysical features like 3 and 4 member rings and reproduces the correct local environment of the carbon atoms. Using a ring clustering method we found that the molecular models contain some defective graphene segments. Apart from the graphene segments, there are many carbon atoms which do not belong to any graphene segments and are arranged in a chain like fashion. We also studied the adsorption of Argon in our molecular models. The adsorption isotherms are found to be typical of microporous solids for both the models. The simulated and experimental isosteric heat of adsorption are also in very good qualitative agreement for both the samples. We are now developing molecular models for a bigger box and future study will involve molecular dynamics simulations in these models to understand the diffusion phenomenon in these materials.

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REFERENCES

- 1) Gregg SJ and Sing KSW, *Adsorption, Surface Area and Porosity (2nd edition)* pp. 3-12, Academic Press, London, 1982.
- 2) McGreevy RL, Pustzai L, *Mol. Sim.* **1**, 359-67 (1988).
- 3) Jain SK, Fuhr J, Pellenq RJ-M, Pikunic J, Bichara C, Gubbins KE. *Stud Surf Sci Catal* (in press)
- 4) Pikunic J, Clinard C, Cohaut N, Gubbins KE, Guet JM, Pellenq RJ-M, Rannou I, Rouzaud J-N *Langmuir*, **19** (20), 8565-82 (2003)
- 5) Jain SK, Gubbins KE, Pellenq RJ-M, Pikunic J. *Langmuir*; (submitted)
- 6) Opletal G, Petersen T, O'Malley B, Snook I, McCulloch DG, Marks NA, Yarovsky I. *Mol Sim* **28** (10-11), 927-38 (2002)
- 7) Petersen T, Yarovsky I, Snook I, McCulloch DG, Opletal G. *Carbon* **42**, 2457-69 (2004)
- 8) Brenner DW. *Phys Rev B* **42** (15), 9458-71 (1990).
- 9) Tersoff J. *Phys Rev Lett*, **61**, 2879-82 (1988).
- 10) Rosato V, Lascovich JC, Santoni A, Colombo L, *International Journal of Modern Physics C* **9**, 917 (1998).
- 11) Jain SK, Gubbins KE. *Langmuir*; (submitted).
- 12) Franzblau DS. *Phys Rev B*, **44** (10), 4925-30, (1991).
- 13) Gelb LD, Gubbins KE. *Langmuir*, **15**, 305-8 (1999).
- 14) Pikunic J, Llewellyn P, Pellenq RJ-M, Gubbins KE. *Langmuir*, **21**, 4431-40 (2005).