

MODELING AND TEXTURAL ANALYSIS OF POROUS CARBONS USING MOLECULAR SIMULATION

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Abstract

We present realistic molecular models of 2 disordered porous carbons using a simulation protocol based on Reverse Monte Carlo which incorporates an energy constraint. We use the empirical bond-order potential developed by Brenner to model the interactions and between carbon atoms. The simulated and experimental radial distribution functions for both the carbon samples are in good agreement. The models also capture the correct chemistry of the carbon atoms, depending on their local environment. Moreover, 3 and 4 member carbon rings, reported in the literature for many modeling studies of carbon, are absent or extremely rare in our final structural models. These small member rings are high energy structures and are believed to be an artifact of the original RMC method.

Introduction

Porous carbons are disordered materials with heterogeneous pore structures. In recent times, reconstruction methods have been popular to develop realistic molecular models of these materials. In this approach a 3D structural model is built that is consistent with a set of experimental data. Reverse Monte Carlo (RMC) (McGreevy and Pustzai, 1988) is one such reconstruction method, in which the molecular model is built to match experimental structure factor data from X-ray or neutron diffraction.

RMC is a fitting procedure in which (subject to some constraints) the model is adjusted to best fit $g(r)$ from experiment. In a previous work (Jain et al, 2006) we studied the stability of the models obtained from a constrained RMC procedure (Pikunic et al, 2003) 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 method (Jain et al., 2006), 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. We used our simulation protocol (Jain et al., 2006) to develop molecular models for three porous carbons obtained from saccharose, previously used by Pikunic et al. (Pikunic et al, 2003) and named CS400, CS1000, and by Jain et al. and named CS1000a (Jain et al., 2005). In this work we use the HRMC method to develop molecular models of two carbon samples named TAC and UMC, obtained from Mead-Westvaco company, of varying density.

Simulation details

The Reverse Monte Carlo method was initially proposed by McGreevy and Pustzai (McGreevy and Pustzai, 1988). 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

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

where S_{sim} is the structure factor for the model material and S_{exp} is the experimental structure factor.

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 (Brenner, 1990). The probability of acceptance of the new atomic configuration is given by:

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

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 the HRMC procedure described in the previous section to build molecular models for 2 carbon samples named TAC and UMC, of varying density. A box size of 25 Å was used to build the model for UMC and a box size of 30 Å was used to build the model for TAC. The box size were chosen such that the radial distribution function, $g(r)$, goes to 1 at less than or equal to half the box length. The density of both the samples as obtained from Hg porosimetry are: 1.987 g/ml for UMC and 1.151 g/ml for TAC. We build molecular models considering only carbon atoms. The presence of other heteroatoms such as hydrogen and oxygen were neglected. We show a comparison between the experimental and simulated $g(r)$ for both the carbon samples in figure 1.

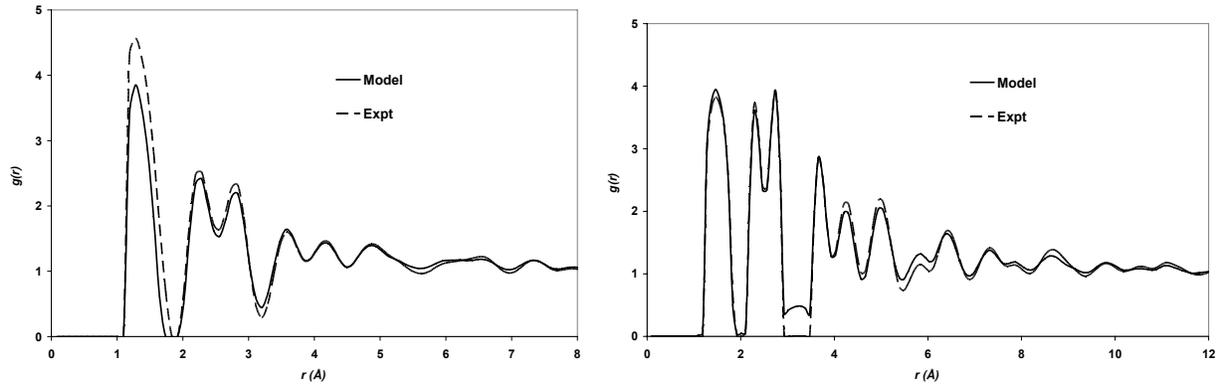


Figure 1: Radial distribution functions of UMC (left) and TAC (right) obtained from experiment and from the model.

We found that the experimental and simulated radial distribution functions are in good agreement. The model underestimates the first peak for the UMC sample, but overall the fit is good. We show a snapshot of the two models obtained using the HRMC method in figure 2. As we can see, the models reveal the disordered nature of the two carbon samples. TAC has a more open structure as compared to that of UMC; this is due to the low density of the TAC sample. We also calculated the ring statistics for both the carbon samples using the shortest path criteria of Franzblau (Franzblau, 1991). We show the distribution of rings in figure 3. Both the samples contain mostly 5, 6 and 7 membered rings. We found that our models contain very few, if any, of 3 and 4 carbon member rings. However, previous RMC studies on carbon have reported a large population of these small rings (Opletal et al, 2002). These small rings are high energy structures and are thus unphysical. These small rings are believed to be an artifact of the original RMC method and are largely absent in our final models due to the presence of the energy penalty term. Upon comparing the ring statistics for both the models we found that UMC has a large population of rings as compared to that of TAC. This is again due to the large density of carbon atoms in UMC, which results in more C-C bonds in UMC as compared to TAC. We also found from the neighbor distribution (not shown here) that most of the carbon atoms in UMC have 3 carbon neighbors and this explains the presence of a large number of rings in UMC.

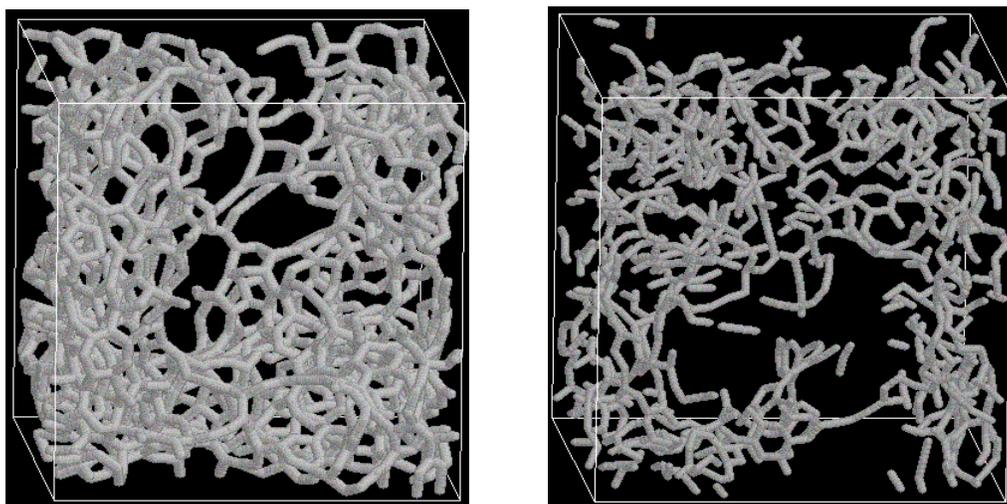


Figure 2: Molecular snapshots of UMC (left) and TAC (right) models obtained from HRMC simulations.

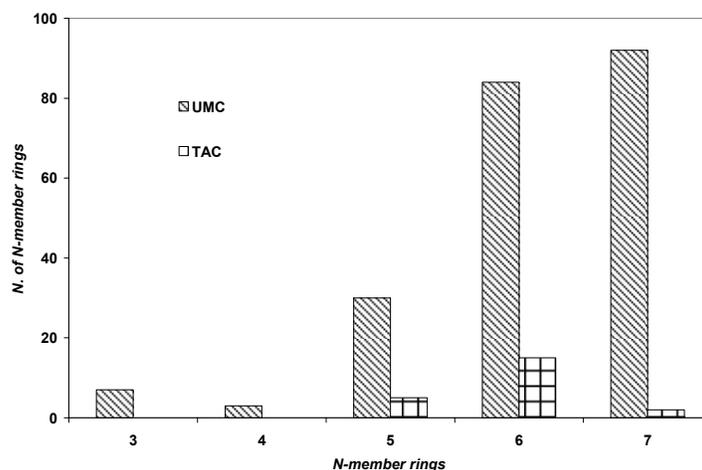


Figure 3: Ring statistics for the UMC and TAC models obtained using HRMC simulations.

Conclusions

In a previous work we developed a method based on the hybrid reverse monte carlo to build molecular models of porous carbons. We used our method to successfully build molecular models for 3 carbon samples obtained from saccharose coke. In this work, we have used the HRMC method to build molecular models of two carbon samples of varying density. We found that the radial distribution function for both the models obtained from simulations match well with that of the experiments. The snapshots of the two models reveal the disordered nature of these carbons. Upon calculating the ring statistics we found that our models contain very few, if any, of 3 and 4 member carbon rings which are high energy structures and unphysical. Future studies will focus on characterizing these carbon samples by (a) calculating the pore size distribution and (b) studying the adsorption of simple gases like argon and nitrogen in these models.

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