

CARBON REPLICA FROM ORDERED MESOPOROUS SILICA TEMPLATE USING GCMC SIMULATIONS

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Abstract

We present a Grand canonical monte carlo study to obtain carbon replica from a silica template. Many experimental studies have been reported on obtaining carbon replica using different templating materials like SBA-15, MCM-41, Zeolites etc. The formation of these templated carbon is a two fold process. A carbon rich precursor in vapor or liquid phase is first deposited inside the porosity of the matrix template. The adsorbed precursor is then carbonized by heating at a high temperature in an oxygen free environment to produce a carbon-matrix composite. Finally, the matrix is removed by treating with an acid and the carbon replica is obtained. In this work we develop molecular models of the carbon replica by adsorbing carbon vapor in the porosity of template matrix using Grand Canonical monte carlo simulations. The carbon-carbon interaction is modeled using the bond order potential developed by Brenner. The matrix-carbon interaction is modeled using the PN-Traz potential. We obtain carbon rods by adsorbing carbon in a model MCM-41 pore. These carbon rods are then used to make simple models for CMK-1 and CMK-3. Preliminary results for the argon adsorption in model CMK-1 and CMK-3 materials is also presented.

Introduction

There has been a growing interest in mesoporous carbons with controlled pore size distribution in the last few years. Nanocasting, using highly ordered mesoporous materials (like silica) has brought forward incredible possibilities in preparing novel mesostructured materials (Yang and Zhao, 2005). Periodic mesoporous materials with variable compositions and controllable morphologies have been receiving much attention because of their versatile uses in separation, catalysis, nanoreactors and sensors. Recently, progress in the study of mesoporous carbons synthesized from periodic silica templates has been achieved (Ryoo et al., 1999); the pore size of these materials can be tailored by using appropriate templates. These carbon materials offer mechanical and thermal stability, high pore volume, electrical conductivity and useful surface properties, and applications include adsorption of large molecules, catalysts in fuel cells and capacitor electrodes. In the preparation of mesoporous carbons a porous material (also named template) is filled with carbon by means of various routes (liquid or gas). The resulting host/carbon materials are then chemically treated to selectively remove the template, which results in a carbon replica of the original template used. Templated synthesis of ordered carbons can be done via volume-templated or surface-templated carbons (Kruk et al., 2003). In the first case, the entire void space of the template is infiltrated with carbon, whereas in the second case, carbon is introduced as a film on the surface of the template. CMK-1 (Ryoo et al., 1999) is an example of volume templated carbons. CMK-5 carbon (Joo et al., 2001)

which consists of 2-D hexagonally ordered carbon pipes is an example of surface templated ordered mesoporous carbon.

Apart from the experimental studies, very few simulation studies has been attempted to model these materials and thus to understand the adsorption behavior in these carbon replicas. In a previous work (Ohkubo et al., 2002), a rod-aligned slitlike pore (RSP) model was used to study the adsorption of nitrogen and supercritical methane in CMK-1. This model is similar to the slit pore model; the only difference is that instead of the infinite graphite walls, the authors used carbon rods placed side by side and adsorption takes place in the region between the two layers of carbon rods. The authors noted that the RSP model was not realistic enough to describe the detailed adsorption mechanism of nitrogen on CMK-1 in a quantitative way. In this work we present a method to obtain carbon rods and carbon pipes by adsorbing carbon vapor from the gas phase in a single MCM-41 pore using GCMC simulations. In a recent work, Roussel et al. (Roussel et al., 2005) obtained replica of zeolites by doing carbon adsorption in the pores of the zeolites. They used a tight binding framework to model the interaction between the carbon atoms. However, the tight binding method is computationally expensive and cannot be used to obtain mesoporous carbons involving thousands of carbon atoms. Here we used the empirical REBO potential (Brenner, 1990) to model the carbon-carbon interaction. This allows us to simulate thousands of carbon atoms within the computing limits. We obtain carbon rods by adsorbing the carbon vapor in the total pore volume of the MCM-41 pore and the carbon pipes are obtained by adsorbing carbon as a film on the surface of the MCM-41 pore. We then used these carbon rods to make simple models of CMK-1, CMK-3.

Simulation details

In this work, we present some of the carbon nanostructures obtained by adsorbing carbon vapor in the porosity of a single MCM-41 pore of diameter 28 Å. We obtained the carbon structures via two routes. In one route we obtain carbon rods by adsorbing carbon in the total pore volume of the MCM-41 pore. In the second route, we adsorb carbon as a film on the silica pore surface to obtain carbon pipes. We change the silica matrix – carbon interaction, the temperature and the chemical potential to obtain carbon rods or carbon pipes of different diameters and wall thickness.

The MCM-41 pore model

The MCM-41 pore was obtained by carving out a regular cylindrical pore of radius R_0 in an atomistic block of cristobalite (a non porous silica mineral) following the method first introduced by Pellenq *et al* to prepare numerical sample of nanoporous silica materials (Pellenq et al., 2000). To mimic the pore surface in a realistic way, the Si atoms which are in an incomplete tetrahedral environment were removed. In a second step all oxygen atoms that are nonbonded were removed. This procedure ensured that the remaining silicon atoms have no dangling bonds and the remaining oxygen atoms have at least one saturated bond with a Si atom. Then the electroneutrality of the simulation box was ensured by saturating all oxygen dangling bonds with hydrogen atoms. The hydrogen atoms were placed in the pore void, perpendicularly to the pore surface at a distance of 1 angstrom from the closest unsaturated oxygen atom. Then all of the Si, O and H atoms were displaced slightly and randomly in order to mimic an amorphous silica surface. The porous structure was further relaxed by performing monte carlo simulations in the NVT ensemble at a high temperature. More details regarding the MCM-41 pore model can be found here (Coasne et al., 2006). A snapshot of the top and side view of the pore is shown in figure 1.

The adsorbate-silica and adsorbate-adsorbate potential energy

The interaction between adsorbate (the carbon atoms) with silica matrix is assumed to be weak and in the physisorption energy range. The interaction energy was calculated using the PN-Traz potential, a simplified version of the original PN-type potential function as reported for adsorption of rare gases and nitrogen in silicalite-1 (Pellenq and Nicholson, 1994). The interaction between the carbon atoms is modeled using the REBO potential. The REBO potential takes into account the chemical bonding between the carbon atoms depending on the local environment of each carbon atom.

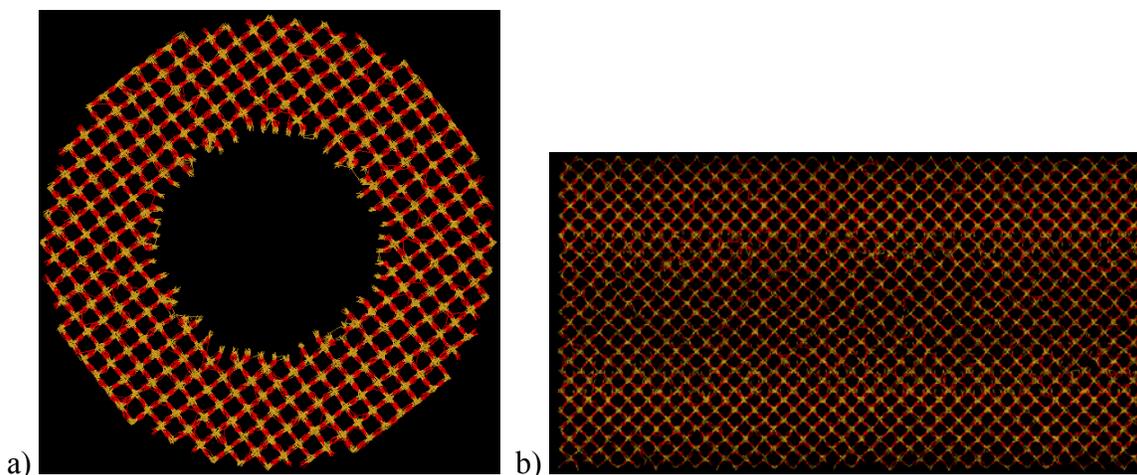


Figure 1. The top view (a) and side view (b) of the MCM-41 pore.

Results

The carbon materials were obtained by doing carbon adsorption from a vapor phase in the pore of the MCM-41 pore. The MCM-41 pore is a cylindrical pore with surface corrugation and roughness. We obtain carbon rods and carbon pipes of different diameters and wall thickness by changing the fluid-wall interaction, temperature and the chemical potential. After the carbon adsorption in the MCM-41 pore, the silica template is removed and the resultant carbon structure is relaxed in the NVT ensemble at high temperature using monte carlo simulations. We found that these carbon rods and carbon pipes obtained are not smooth and are disordered at the local level. Moreover, the pore outer surface as well as the inner pore surface (in case of carbon pipes) are rough and corrugated. We show sample snapshot of a carbon rod in figure 2.

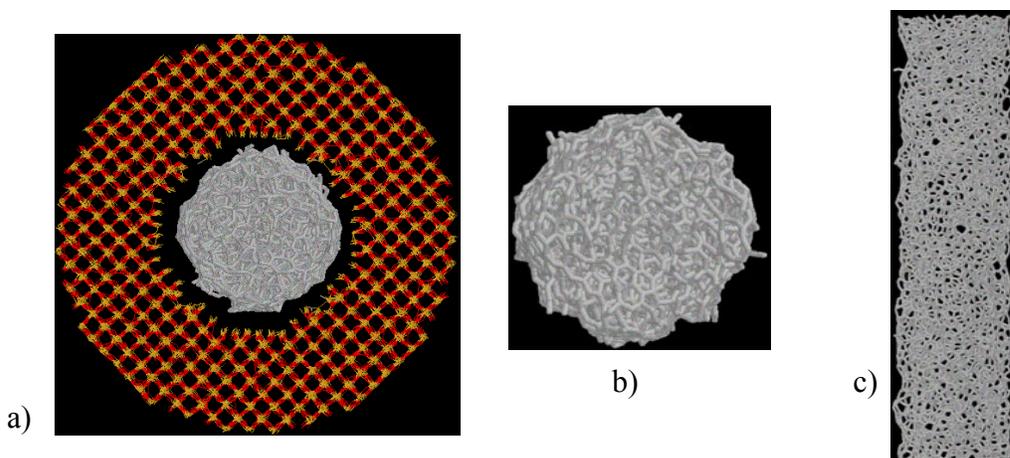


Figure 2. (a) Carbon rod obtained by doing carbon adsorption in the MCM-41 pore. Carbon rod obtained after removing the silica template and relaxing the carbon structure: (b) top view and (c) side view.

It is reported in the literature that the CMK-1 material is made up of carbon rods arranged in a cubic lattice and CMK-3 is made up carbon rods arranged in a 2 dimensional hexagonal lattice. We propose the following simple models for CMK-1 and CMK-3. We arrange the carbon rods obtained, in a cubic lattice to obtain a model for CMK-1. Similarly, we arrange the carbon rods in a hexagonal lattice to obtain a model

for CMK-3. However, it is known that in CMK-3 the carbon rods are interconnected by carbon chains, which prevents the structure from collapsing. Thus, it should be noted that our simplified models neglect these interconnections between the carbon rods. We show the models of these materials in figure 3.

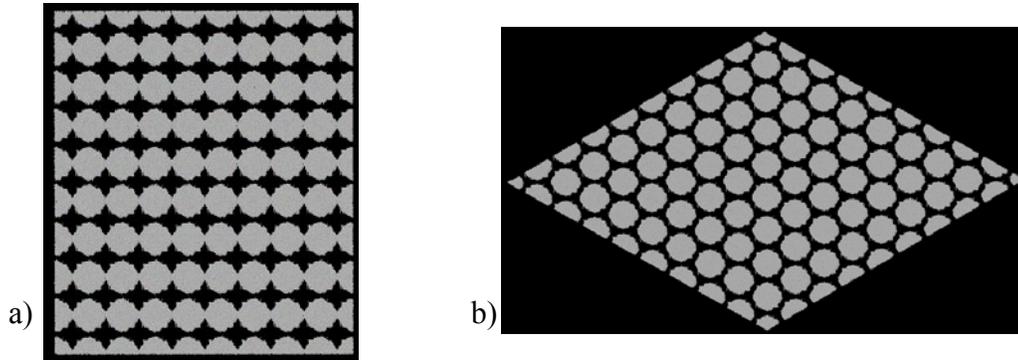


Figure 3. (a) Carbon rods arranged in a cubic lattice to obtain a model for CMK-1 and (b) Carbon rods arranged in a hexagonal lattice to obtain a model for CMK-3.

The diameter of the carbon rods and the distance between the carbon rods can be changed to obtain models of CMK materials with different pore volume and wall thickness. We are studying the adsorption of argon in these CMK models. We present some preliminary results of argon adsorption in one of the CMK-1 and CMK-3 models. In the CMK-1 model, the carbon rods are placed side by side in the horizontal direction and the pore size in the vertical direction is 7.64 \AA . This pore size refers to the distance between the outer surfaces of two carbon rods placed vertically. The carbon rods are assumed to be infinite in the pore axis direction. In the CMK-3 model we arrange the carbon rods in a hexagonal lattice. The pore size (i.e. the distance between two carbon rods in a hexagonal lattice) is 7 \AA . As in CMK-1, this pore size refers to the distance between the outer surfaces of the carbon rods.

In Case of CMK-1, we found that at low pressure the adsorption occurs in the groove between two carbon rods placed horizontally and on increasing pressure the adsorption occurs at the outer surface of the carbon rods and finally at the vapor pressure of argon the total pore volume is filled. We show snapshots of the argon adsorption at different pressures (see figure 4) that gives an idea of the mechanism of the pore filling.

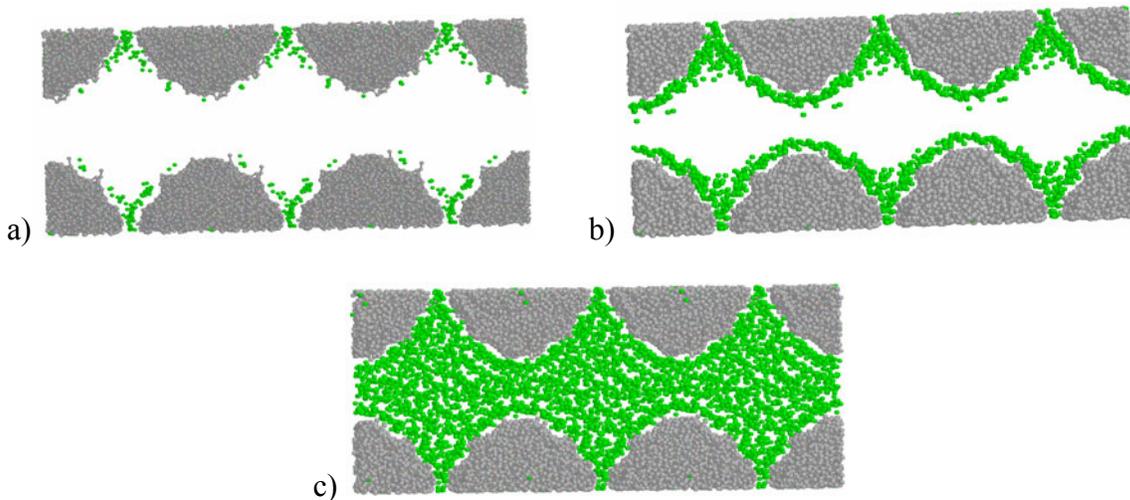


Figure 4. Snapshot of Argon adsorption in a CMK-1 model at (a) $P/P_0 = 0.0001$, (b) $P/P_0 = 0.01$ and (c) $P/P_0 = 1$. The argon atoms are colored in green and the carbon matrix is in grey color.

In case of CMK-3, we found that the adsorption first occurs around the carbon rods at some selective places, which have high attractive energy, at low pressure. Thus, the adsorption on the outer surface of the carbon rods is not uniform, which is expected since the carbon rods are not smooth. As the pressure is increased, a thin film of argon is formed covering the outer surface of the carbon rods. At higher pressure, the total pore volume is almost filled with argon. Figure 5 shows a sketch of the adsorption phenomenon occurring in the CMK-3 model. We found that the pore filling occurs at a relatively lower pressure in this CMK-3 model as compared to that of the CMK-1 model reported above.

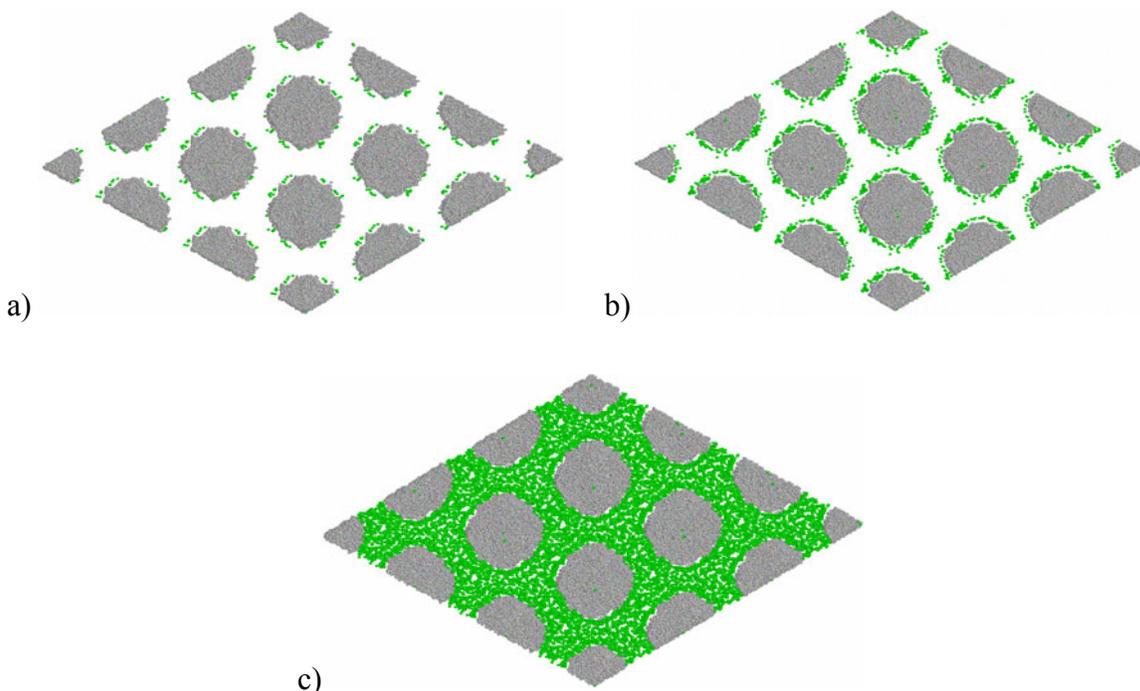


Figure 5. Snapshot of Argon adsorption in a CMK-3 model at (a) $P/P_0 = 0.0001$, (b) $P/P_0 = 0.001$ and (c) $P/P_0 = .01$. The argon atoms are colored in green and the carbon matrix is in grey color.

Conclusions

We have presented simple models for mesoporous carbons obtained via the templating procedure of silica, by simulating the carbon adsorption in the vapor phase inside a MCM-41 pore. Carbon rods and carbon pipes were obtained by varying the silica- carbon interaction strength, the chemical potential and the temperature. The resultant carbon structures, whose morphology was governed by the MCM-41 pore, were found to be disordered, in terms of the arrangement of the carbon atoms. We then used these carbon rods to obtain crude models for CMK-1 and CMK-3. However, our model for CMK-3 does not take into account the interconnections between the carbon rods, present in a real CMK-3 material. Currently we are studying the adsorption of argon in these CMK models to understand the adsorption phenomenon in these materials. We presented some preliminary results for argon adsorption in one of the CMK-1 and CMK-3 models and found that the pore filling occurs at a lower pressure in the CMK-3 model as compared to the CMK-1 model. Full adsorption isotherm for these models will be presented in a subsequent study.

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