Supplementary information for 'Effect of pore structure on the selectivity of carbon materials for the separation of CO₂/H₂ mixtures: New insights from molecular simulation'

K. Vasanth Kumar* and Francisco Rodríguez-Reinoso

Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica Universidad de Alicante, Spain.

*E-mail: vasanth@ua.es

1. Simulation details

In this study GCMC simulations were used to study the adsorption behavior of CO_2 on nanoporous materials as detailed in standard references. ¹⁻⁵ The grand canonical ensemble allows the equilibriation of a gas phase with a confined fluid phase and in that sense is an ideal scenario for studying adsorption. In GCMC, the chemical potential (related to the activity or fugacity), the temperature and total volume of the system are kept constant and in equilibrium with a bulk phase (with no adsorbent present) at the same chemical potential and temperature. The total number of fluid molecules in the system is allowed to fluctuate and its statistical average is one of the relevant quantities of interest. In our simulations we replaced the chemical potential by the more convenient variable activity, ζ_i as employed by ⁵⁻⁶

$$\zeta_i = \frac{\exp(\mu_i / kT)}{\Lambda_i^3} \tag{1}$$

where Λ_i is the de Broglie wavelength, which includes the contributions from the translational and rotational degrees of freedom and *k* is the Boltzmann's constant. The use of activity has the computational advantage that in the ideal gas limit it corresponds to the number density while at intermediate densities it can be related to the pressure by simple analytical expressions. The readers are referred to Muller ⁷ for details on the implementation of the simulations. As the pressure in this study may be in excess of 10 bar, in order to obtain the relationship between the activity and the pressure we performed a set of additional GCMC simulation at a fixed temperature spanning the range of activities of interest in a simulation cell without any adsorbent, thus obtaining the corresponding average bulk density. The pressure is then found from an appropriate equation of state at the corresponding density and temperature.

Intermolecular potential functions for small quadrupolar molecules can range from the simple representations, such as Lennard-Jones (LJ) representations, taking into account in an average way isotropic repulsion and dispersion terms. ⁶ In this work, CO₂ is represented by a two-center (dumbbell) Lennard-Jones molecule with a fixed rigid bond length, L, and a point quadrupole of strength, Q. The fluid-fluid parameters are taken directly from the parameterization of Vrabec et al ⁸ and give a quantitative representation of both the equilibrium vapor-liquid coexisting bulk densities and the P-V-T behavior of the fluid phases. Following the work of Cracknell, ⁹ H₂ is modeled as a two-site Lennard-Jones fluid with a fixed bond length. The intermolecular potentials are detailed in the manuscript.

All solid structures, described in the next section, are composed of spherical sp² hybridized carbon sites fixed in space in the simulation cell with the same parameters as Steele ¹⁰ potential, $\sigma_{CC}=0.340$ nm and $\varepsilon_{CC}=28.0$ K. The fluid-solid interactions are taken to conform to Lorentz-Berthelot rules, viz. $\varepsilon_{sf} = \sqrt{\varepsilon_{ss}\varepsilon_{ff}}$, $\sigma_{sf} = (\sigma_{ss} + \sigma_{ff})/2$. The subscripts s and f refer to the solid atoms and fluid molecules, respectively.

Monte Carlo simulations were run up to 10^7 configurations. The first 5.10⁶ configurations are used to ensure the equilibrium while the latter 5.10⁶ configurations are used to calculate the ensemble averages. The usual periodic boundary conditions were applied in all three coordinate directions in order to mimic infinite size systems.

2. Nanoporous structures

In the following sub-sections, four nanoporous carbon model structures (Fig s1) used in this work are described:

The slit-shape pore model used in this study is assumed to be composed of three stacked planes of graphite separated amongst them by an interlayer distance of 0.335 nm. The planes are infinite in size (due to the boundary conditions) and placed on each side of the pore. This slit pore can be approximately modeled using the Steele ¹⁰ potential, and in this study, no significant differences were seen amongst the two (explicit and integrated) potentials. The slit pore model used in this study has a fixed pore width of *H*, 1.5 nm. In this study, we define the pore width, *H*, as the distance between the centre of the carbon atom on one wall to the centre of the carbon atom on the opposite pore walls. It is important to mention that the definition of the pore width is ill-defined. A second

commonly employed definition of the pore width considers the apparent distance between the surfaces of the walls. Upon the assumption that this corresponds to the point of null potential energy at the wall, one may define the actual pore width, H' as $H - \sigma_{ss}$, where 's' refers to the solid atom.

An ideal model for carbon nanotube bundle consists of parallel single-walled carbon nanotubes (SWCNT) with equal diameter *D*. The carbon nanotube structure used in this study contains six zig-zag (16, 0) nanotubes of internal diameter of 1.255 nm (measured from the centre of atoms). The diameter of the nanotube was chosen to be as commensurate with the other structures. Only adsorption inside the nanotube was considered, i.e., the interstitial sites and the endohedral adsorption are not considered here. The effect of interstitial adsorption should be considered or dealt separately as the storage capacity in interstitial regions may be significant. Adsorption in nanotubes will be affected by other factors not considered here such as the distance between the tubes, the geometry of the tubular arrangements and/or the polydispersity of the samples.¹¹

The *in silico* generated random porous carbon structure that can be taken as a model of real carbons was constructed from a collective of flat coronene-shaped graphitic basic units made up of 24 carbon atoms. The random structure was obtained by placing a number of these carbon-building units in a simulation box avoiding overlapping of the carbon units. ¹² There are no bridges formed between the structures and they are artificially fixed in space within the cell. Obviously, a number of realizations of this structure can be obtained by different placements of the basic units; however, the results (for the same density of basic units) seemed to be reasonably independent of the actual details. A unique realization, depicted in Fig s1 was selected for the adsorption studies presented here on the basis of attempting to broadly have similar morphological properties as the other, better defined structures (nanotubes and slits). Each individual carbon centre has the same properties (C-C spacing and intermolecular potentials) used throughout this work.

Hypothetical three-dimensional carbon foams have been described by the group of Yakobson ¹³⁻¹⁴ by conceptually fusing SWCNT of similar diameters in order to obtain a three-dimensional porous network. The particular carbon foam (Fig 1s), was obtained by welding an armchair (10,10) with a zigzag (17, 0) SWCNT. The unit cell of carbon foam

structure contains 970 carbon atoms and each carbon atom is defined by a single LJ site in the same spirit as the other models.



Fig s1: Unit cells of the nanoporous carbons: (a) slit, (b) nanotubes, (c) random porous structure and (d) foam

3. Characterization of carbon structures

It is expected that the structure and shape of the pores will affect the adsorption properties of the carbon depending on the fluid molecules and simulation conditions (temperature and pressure). Thus, in order to analyze and compare the effect of pore geometry on the selectivity, we estimated two parameters that could reasonably be used to characterize the difference between the studied pore geometries: the accessible surface area and the available pore volume. These parameters were estimated using the geometrical method proposed by Duren et al¹⁵ to calculate the accessible surface area and volume. This method relies on a Monte Carlo integration technique where a probe molecule equal to the LJ molecular size of fluids of interest (in the present case is equal to the size of H₂ or CO₂) is 'rolled' over the framework surface. This technique involves random insertion of probe molecules around each of the framework atoms and check for overlap with other framework atoms. The fraction of the probe molecule that did not overlap with other framework atoms was then used to calculate the accessible surface area.¹⁵ Thus all the values obtained are applicable for molecular diameter probe molecule equal to the size of hydrogen or CO₂ and obviously they would vary if other fluid molecules were considered. The accessible surface area and the pore volume of the carbon structures were estimated using a single site LJ atom model and hard sphere potential (for H₂: σ = 2.96 Å; for CO₂: σ = 3.648 Å), in accordance with the procedure adopted in the work of Duren et al¹⁵. The determined accessible surface area and the ratio of accessible pore volume to total volume of the studied carbon structures obtained using the geometrical method for the case of both hydrogen and carbon dioxide are give in Table 1s. In Table 1s, the surface area is expressed in terms of available surface area per unit of mass of adsorbent (m^2/g) . The mass of adsorbent was determined considering the carbon atoms in the pore structures. In Table 1s we also show the porosity, ϕ , of the samples, expressed as the ratio of accessible volume to total unit cell volume and the gravimetric density of each structure.

In the case of RPC, the surface area is extremely large (> $3500 \text{ m}^2/\text{g}$), as each carbon atom of the coronene-shaped graphitic unit is accessible on both sides to the fluid molecules during the adsorption process. It is important to note that this is a hypothetical structure, with no connectivity amongst the segments. In the case of nanotubes, the surface area is smaller than expected as we considered only endoadsorption in the nanotubes. The surface area of the foam structure lies in between them. In the case of a slit-pore, the mass is ill defined, as the cell has an arbitrary number of graphene layers which do not take part in the adsorption process. The surface area per unit mass of slit-pore in Table 1s will be three times larger if we consider only one third of the carbon atoms, as two of the three layers of graphene next to each pore wall is inaccessible for the CO_2 molecules.

While considering the available pore volume, it can be observed from Table 1s that the random structure has the largest accessible pore volume for the molecular size of H₂ or CO₂, followed by slit, foam and nanotubes. In the case of carbon foam, we noticed that their three dimensional porous network provides a combination of high surface area and free volume when compared to other structures. All the values obtained are only applicable for molecular diameter probe molecule equal to the size of the fluid molecules of interest here, and this these values cannot be generalized to other molecules. In order to have more insight about the studied pore structures and to compare the physical characteristics of the studied pore geometries, we estimated the pore-size distribution of the studied pore structures. In the case of nanotubes and in slit-pores, it would be easy to estimate the pore-width analytically, however in the case of RPC and foam structures, it is far from trivial. In these structures, we estimated the pore-size distribution employing the procedure developed by Gelb and Gubbins ¹⁶ and later applied for the first time for MOF structures by Sarkisov and Harrison.¹⁷ Here a test point 'a' is randomly placed in the simulation cell and tested for the overlaps with the structure atoms, making sure that the point is not inside an atoms. If no overlaps are observed, the porous space is probed to find the largest sphere that contains point 'a' and does not overlap with the atoms of the structure. The normalized distribution corresponds to the monotonically decreasing cumulative pore volume function, $V_p(r)$, which is the volume of the void space that can be covered by spheres of radius 'r' or smaller. The derivative $dV_p(r)/dr$ is the pore-size distribution (PSD) and can be obtained via numerical differentiation of $V_{p}(r)$. In the present work, the pore-size distribution corresponds to the use of probe molecule with diameters up to 3 nm.

Figure 2s shows the PSD of RPC and foam structures obtained using the above procedure, along with that for the nanotubes, placed here as a comparison. The PSD of the nanotube peaks sharply at H' = H- σ_{CC} = 0.91 nm, as expected. In the case of random carbon pores, we find that they present a broad pore size (H') distribution ranging from 0.17-1.55 nm with considerably sharp peaks at 0.71 and 0.91 nm, indicating a dense microporous carbon. The pores of this size can hold roughly 2-3 layers of hydrogen and carbon dioxide molecules, which is comparable to the pore width of the other ideal pore models (slit and nanotubes) studied. The pores of effective pore size, H', < 0.29847 nm in the random structure would sterically exclude the CO₂ molecules but they can sufficiently hold one layer of H₂ molecules. The PSD plot, as a whole, suggests that the RPC is a suitable structure for modeling complex carbons.

In the case of carbon foam, obtained by welding (10,10) with (17,0), the PSD is bimodal and much more discrete than the random structure, as the welding process retains the pore sizes of the parent nanotubes, but it also gives rise to new pores of different sizes. The PSD of foam shows that contain predominantly pores of sizes, H', 0.85, 1.6, 1.8 and 2.1 nm, in general larger than the pores available for the other structures. The larger pore of 2 nm corresponds to the center of the tube crossings where the structure is more open, akin to the cages of zeolitic materials. The large amount of pores, H', in the range of 1.15 and 2 nm clearly indicates that the carbon foam can hold multiple layers of hydrogen or carbon dioxide molecules depending on the temperature and pressure.



Fig 2s: Pore size distribution of random structures, foams and nanotube

Pore		free volume,cm ³ /g		surface area, m ² /g		Porosity, ø	
Structure	N _C	CO ₂	H_2	CO ₂	H_2	CO ₂	H_2
foam	970	0.881	0.963	2434	2505	0.5	0.547
nanotube	4608	0.083	0.586	623	702	0.09	0.120
random	2280	0.44	0.586	3771	4428	0.236	0.315
slit-pore	6048	0.177	0.193	459	460	0.253	0.275

Table 1s: Characteristics of nanoporous structures

 N_C = number of carbon atoms in the studied carbon frameworks

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