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In silico designed microporous carbons

Aleksandra Gonciaruk, Flor R. Siperstein *

School of Chemical Engineering and Analytical Science, The University of Manchester, M13 9PL, United Kingdom

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ABSTRACT

This work presents a computational study on the packing of three-dimensional carbon nanostructures and their effect on gas adsorption properties. We show that it is possible to obtain intrinsically microporous materials without specifying structural properties such as surface area or pore size distribution by packing individual graphene platelets connected at a contortion site. The resulting structures can potentially represent disordered carbons and provide understanding of the relationship between pore structure and adsorption performance. The calculated CO_2/CH_4 selectivity of these materials at the zero coverage selectivity can be as high as 25, whilst at low finite pressures (0.05 bar) is between 6 and 10, which is comparable with what is expected for most carbons. We compare the results to the ones obtained from a simple slit pore model and highlight the importance of pore morphological complexity to adsorption of industrially important gases.

1. Introduction

Activated carbons have been used for thousands of years but an accurate microscopic description of their structure is still a mystery. Controlling their properties is a balance between art and science. Much research has been done in understanding the roles of the precursors and activating procedures, and the use of molecular simulation and reconstruction techniques has provided some insight into the fundamental properties of these materials.

The use of predesigned carbonaceous structures in the synthesis of these materials has been proposed by Müllen's group using an aromatic ring at the centre of the molecule or a tetrahedral carbon with graphene-like arms [1]. The materials proposed by Müllen have a flexible core which is expected to lead to non-porous structures. An alternative is to use a rigid core, similar to the one used in Organic Molecules of Intrinsic Microporosity [2] or Polymers of Intrinsic Microporosity [3] to create an inherently microporous structure. In this work we aim to predict the properties of in silico designed porous carbons using a systematic approach. The carbons are constructed using a well-established methodology to pack molecules that form amorphous materials [4]. The carbonaceous molecules contain a central unit that will be named core, and graphene-like arms that will provide the environment for adsorption. The molecules are designed to allow us assessing the role of core centre as well as the size and shape of the arms. Although the materials shown have not been synthesised to the best of our knowledge, the virtual structures obtained are expected to serve as a starting point to understand the connectivity between twisted and defective carbon sheets, the effect of edges, and packing abilities based on the precursors.

Molecular models of carbons have been studied since the pioneering work of Steele, and the derivation of the 10-4-3 potential for slit pores [5]. The slit pore model has served to characterise porous carbons by inversion of the adsorption isotherms to obtain the pore size distribution. Currently Density Functional Theory (DFT) models to obtain pore size distribution are common practice in most laboratories [6,7].

* *Corresponding author.*
E-mail addresses: aleksandra.gonciaruk@postgad.manchester.ac.uk (A. Gonciaruk), flor.siperstein@manchester.ac.uk (F.R. Siperstein).
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Nevertheless, the slit pore model cannot capture all the properties of activated carbon which possesses great structural and chemical complexity. Significant efforts have been made to construct realistic models of porous carbons. The most physically sound approach is mimetic method that imitates experimental synthesis process. This is achieved using quench molecular dynamic [8,9] where gas or liquid carbon atoms are rapidly cooled simultaneously forming bonds resulting in connected amorphous structures or using canonical ensemble Monte Carlo simulation which evolves amorphous polymer to a disordered sp^2 hybridized carbon by reforming bonds [10]. Another computationally expensive approach is reverse Monte Carlo (RMC) techniques that also reconstructs realistic disordered porous carbons structures by fitting experimental diffraction data of real materials [8,11–16]. Although these methods provide reasonable model structures for a specific material, it is difficult to generalise the information obtained from the simulations to a broader class of materials. Using well-defined building blocks or periodic structures as part of the model material complements the knowledge gained from very specific models. The amorphous structure of nanoporous carbons can also be represented by fullerenes, bundles of carbon nanotubes or a foam-like hypothetical C_{168} Schwarzite for surface morphology, for adsorption and diffusion studies [17–19]. A alternative approach that has gained significant attention consists in packing of idealized structures: structureless platelets [20,21], atomistically described platelets [22], the construction of virtual porous carbons [23]. Carbon models formed by unconnected building blocks lack some of the features that make an amorphous carbon self-standing material thus the method requires density, surface area and/or pore size distribution input data. We are particularly interested in exploring the latter approach of individual fragment packing but we introduce connectivity between them to obtain free standing material without the need of structural data.

This work follows on the idea of packing individual molecules to describe a carbonaceous material, but we do not explicitly specify the porosity (surface area or density of the material), which is necessary when using simple molecules like coronene [22]. The equilibrium structure of coronene would not be a porous carbon, but stacks of molecules packed together. We are able to obtain porous structures without imposing a predefined surface area as a result of having rigid contortion sites as part of the designed molecules. Although real carbon materials may not be equilibrium structures as prepared, ageing of the materials is expected to move them towards an equilibrium structure, therefore understanding the differences between materials with connected and unconnected graphene platelets can help understanding ageing of these materials.

This paper assess properties of carbonaceous materials obtained from packing pre-designed three-dimensional (3D) molecules and compares them with the carbon model proposed by Sarkisov group [22]. We test the validity of using a simple slit pore model with the calculated pore size distribution on the model material to predict the CO_2 and CH_4 adsorption at low pressures, which highlights the importance of platelet edges and various pore shapes observed in different materials.

2. Methodology

2.1. Preparation of carbon materials

Models were constructed and graphical displays generated using Material Studio software (Accelrys Inc.). Graphene arms were created in planar form by connecting six-membered carbon rings. The arms were then connected through two different centres inspired by triptycene ([2.2.2]propellane, hereinafter *trip*) and cyclotricatechylene (hereinafter *CTC*) (Fig. 1). The spherical structure of *trip* possesses rigid threefold symmetry that keeps graphene arms separated in 3 dimensions, whilst *CTC* centre is very flexible, thus allows for greater freedom for intramolecular graphene arms to form a single stack. Graphene arms were created connecting six membered aromatic carbon rings. The edge carbon atoms of the graphene were saturated by connecting hydrogens. Four different arms were constructed (Fig. 2): small (S), medium (M), large (L) arms of disk shape and medium size ribbon-like arm (M-ribbon). The carbon models as well as carbon dioxide and methane are described fully atomistically. Interactions between atoms are described using the Dreiding forcefield [24] for packing. This forcefield has been used previously to model structurally and chemically similar materials known as Organic Molecules of Intrinsic Microporosity [25], porous aromatic frameworks [26]. Five different materials were obtained by connecting arms and cores: S-trip, M-trip, L-trip, M-CTC and M-trip-ribbon.

2.2. Compression methodologies

The structures were packed in a low density box of 60 nm^3 with periodic boundary conditions. The number of molecules varied between the systems to achieve a target density 0.49 g cm^{-3}. Three simulation boxes were constructed for each of five model carbon structures obtain averaged results. The systems were then compressed using different packing procedures. The first packing method is based on the 21 step compression and decompression scheme described in Larsen et al. work [4]. We used slightly modified procedure to speed up the packing process, where all the NVT steps at 300 K were half as long as what was proposed initially [4]. Another method involves more rapid and less drastic compression pressure. The scheme is provided in Table 1. Molecules have more freedom to move at the first stage, where temperature is kept at 600 K and initial large volume is constrained. After this extended step system is cooled down and compressed

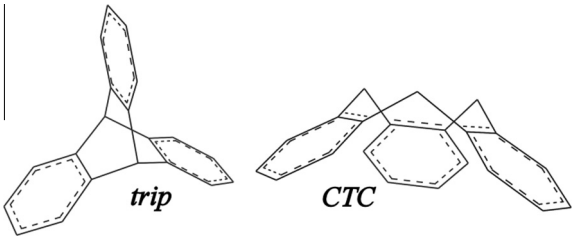

Fig. 1 – Centres of model carbons.