Second-generation kernel for characterization of carbonaceous material by adsorption

Sebastião M.P. Lucena[*], José C.A. Oliveira, Daniel V. Gonçalves, Pedro F.G. Silvino

Dept. Eng. Química, Grupo de Pesquisa em Separações por Adsorção — GPSA, Universidade Federal do Ceará, Campus do Pici, Bl. 709, 60455-760, Fortaleza, CE, Brazil

ABSTRACT

A complete Monte Carlo heterogeneous kernel of N_2 adsorption isotherms for activated carbon characterization was developed based on experimental insights from the carbon oxidative etching mechanism. The local isotherms of the kernel were split into four degrees of etching. With this new kernel, we analyzed microstructure evolution with burn-off and surface discrimination, two important carbon characterization problems. New atomic-level information of the development of porosity as the microstructure evolves with burn-off was obtained. This same kernel can differentiate between graphitized and non-graphitized surfaces, a promising new feature of such a kernel, creating an opportunity to apply adsorption as a large-scale method for the characterization of high-end graphene devices. The study also highlights that for both tested applications (microstructure evolution and surface discrimination), a heterogeneous multikernel, as opposed to the standard single kernel available in commercial equipment, is essential to improve characterization.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Perfect homogeneous slit-pore models were used in the first molecular simulation studies relating to nanoporous carbons in 1985 and 1986 [1,2]. In the early 1990s, the combined approach of nonquantum density functional theory (DFT) or grand canonical Monte Carlo (GCMC) simulation and homogeneous slit-pore model became the standard method for obtaining a pore size distribution (PSD) in the micropore to mesopore range [3]. Using a simulated kernel of local isotherms in a series of independent pores, the PSD is obtained by deconvolution of the generalized adsorption integral (GAI) (Equation S1). We will call these collections of isotherms obtained with homogeneous models "first-generation kernels."

Despite the better results with the new methodology compared with the earlier empirical methods [4], these first-generation kernels have a consistently low population of pores around center-to-center pore size, $H_{cc} = 12.5$ Å, and small steps (S-shape) in the theoretical isotherms, which are not observed in sorption isotherms obtained experimentally. This drawback was associated with the lack of chemical or geometrical heterogeneity of the pore walls, as observed in 1998 by Olivier [5]. Several suggestions for including heterogeneities were proposed [6—10], however, it was only in 2009 that Neimark et al. [11] formally incorporated a heterogeneity proposal into a complete DFT-based kernel named QSDFT (quenched solid density functional theory). Jagiello and Olivier [12] presented another complete heterogeneous kernel in 2013, also based on DFT (2D-NLDFT). We will refer to any complete collection of isotherms from heterogeneous models as "second-generation kernels."

Several carbonaceous materials have already been investigated with heterogeneous kernels based on DFT [13,14]. The great majority of the studies that use heterogeneous kernels have been used only to obtain the PSD without analyzing the possibility of carbon structure optimization or refinement of the characterization methods. An important exception is the study by Gor et al. [15], where a series of specialized hybrid kernels composed of QSDFT slit and cylindrical pores successfully reproduced the isotherms of N_2 on mesoporous carbons (CMK-3 and 3DOm). The studies by Jagiello et al. [16] and Kowalczyk et al. [17] that built new heterogeneous kernels are other examples. Within the framework of 2D-NLDFT, Jagiello [16] built a kernel of CO_2 and proposed the simultaneous use of CO_2 isotherms at 273 K and N_2 at 77 K to obtain PSDs. Kowalczyk et al. [17] built a GCMC-based heterogeneous kernel with rumpled surfaces. Although it does not consist of a kernel

* Corresponding author.
E-mail address: smlucena@uol.com.br (S.M.P. Lucena).

proposal, it is also worth noting the study by Fan et al. [18], which proposes new geometries for heterogeneous pores, some with a closed end, able to reproduce all hysteresis loops classified by the IUPAC.

A particularity that draws attention in these studies is that all approaches to using heterogeneous kernels are made with only one level of heterogeneity. The use of a single kernel imposes the same degree of heterogeneity on all the analyzed carbonaceous materials. Considering that the activated carbons present different degrees of heterogeneity, to approximate models of heterogeneous pores with the real material, we propose that several levels of heterogeneity need to be incorporated in the kernels. In the same direction of obtaining more realistic kernels, it is also desirable that the procedure for generating heterogeneity must contain elements of the actual process of production of activated carbon. This last directive makes sense because we can improve the fit of the adsorption isotherm by several strategies of introduction of heterogeneity (multiwalled pore [6], rumpled surface [7], corrugated amorphous walls [11], finite pore models [12], random particles over the pore surface [19]), consequently the closeness of the model to the real material can be used as a criterion for choosing a particular strategy to build a kernel.

Shortly after Neimark's study [11], we suggested a strategy to introduce heterogeneity in a homogeneous model [20] inspired by the oxidative etching process (Randomly Etched Graphite model), which takes place during activated carbon manufacture. In this exploratory study, we prove the effectiveness of the etched pores to correct the discrepancies in the isotherm fitting. Instead of DFT, GCMC was employed to perform all the calculations. GCMC has the advantage of being readily applicable to more complicated models of adsorbate molecules and to more complex etched topologies that could be developed. However, in that study, only six isotherms generated by etching two pores of 13.4 and 15 Å were combined with a homogeneous isotherms kernel. A complete etched kernel, that would introduce several levels of heterogeneity, was missing. Such a kernel has to be done with subkernels with four different degrees of etching (0, 25, 50 and 75%), allowing coverage of the wide range of burn-offs of large-scale production processes.

A kernel, with at least four different degrees of etching, raises important questions regarding its practical application: (i) What is the advantage of increasing the complexity of PSD analysis, introducing three more kernels to the preexisting homogeneous kernel? (ii) Considering the trend established by the equipment manufacturers to use only one heterogeneous kernel, would there be real gains in the use of multikernels? Secondarily, in addition to the evidence already described in the literature [10,21—23] that etched surfaces can be reliably used to probe the physical structure of the solid phase in carbons, (iii) what new experimental evidence from studies of oxidative degradation correlate with the etched model? These are some questions that need to be addressed to justify a new complete kernel proposal.

To answer questions (i) and (ii) here, we built three complete etched subkernels (with 22 pores each) and investigated two practical problems that demand careful attention to the characterization methods based on adsorption. One problem was the prediction of the microstructure evolution with burn-off of an activated carbon (essential for optimization of the production processes) and the other was discrimination of surface defects (given the large volume of research on graphene).

Regarding question (iii), we found that new experimental studies motivated by research in graphene [24—26] has confirmed important features of the etched approach and provided independent physical evidence to support it. These studies show that (a) In a monolayer sheet of graphene, the initial step of pit creation is a stochastic process, where inner carbons and edge carbons are equally affected [24] and (b) During controlled oxidative etching of a multisheet graphene sample, the layers are removed in sequence, with the damaged top-layer graphene sheet being completely removed, exposing the second layer to be attacked and so on [26]. These important features are reproduced in the present etched kernel, where only one layer is etched and the process of atom deleting is stochastic.

The paper is structured as follows. Section 2 describes the details of the etched model development and how the isotherms that constitute the new complete etched kernel were obtained. In Section 3, we present the morphology of the heterogeneity introduced in the etched process, how the kernel predicts the microstructure evolution of a series of activated carbons and the ability of the kernel to discriminate surface defects. We show that the multikernel approach (in opposition to single heterogeneous kernels) provides new atomic-level features for a series of activated carbon samples with increasing burn-off. We prove the consistency of the complete kernel as it correctly associates etched pore volumes with the heterogeneity. We also verify that the multikernel approach adequately discriminates carbonaceous surfaces, fulfilling an important void because there are no appropriate kernels for surface discrimination. These results support the fundamental idea that multiple heterogeneous kernels (Monte Carlo- or DFT-based) are essential to narrow the gap between the theoretical model and the real material. Conclusions are summarized in Section 4. Kernels, PSD details and additional N_2 adsorption isotherms are given in Supporting Information.

2. Models and methods

2.1. Carbon and gas models

The collections of local isotherms were obtained from homogeneous and heterogeneous slit-pore models. The homogeneous model consists of walls with three perfect parallel sheets of graphene with dimensions of 40×40 Å^2 (Fig. 1a). The heterogeneous model also has the same walls of graphene except that the innermost layer has its carbon atoms randomly deleted (Fig. 1b) in the proportions of 25, 50 and 75% [20]. As stated in the introduction, the removal of carbon atoms of the innermost layer is performed to introduce heterogeneities into the model. Different trials of the same amount of carbon removal result in very similar isotherms, which represents an advantage of our etching strategy (Section S4).

Following previous studies [12,19,27], we used the united-atom model for the N_2 molecule. We know that the molecule model (atom—atom or united atom) can affect the pore-filling regime and influence the PSD [27—30], however, we intend to be as conservative as possible and employ the same current models used in the local isotherms kernels of the commercial analytical equipment.

We assumed that the repulsive—dispersive forces between fluid molecules and the adsorbent (fluid—solid) and between other adsorbates (fluid—fluid) were described by the Lennard-Jones 12-6 potential (LJ):

$$U(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \tag{1}$$

where ε_{ij} is the well depth, σ_{ij} is the equilibrium diameter, and r_{ij} is the distance between interacting atoms i and j.

The LJ parameters for the N_2 molecule were taken from Ravikovitch's study [27]. The LJ parameters for the carbon atoms were derived from Steele [31] with the energy parameter slightly adjusted to reproduce the experimental isotherms of N_2 on the standard surface of Carbopack F [12]. The cross-LJ terms were