

Description of condensation and evaporation processes in cylindrical-type porous materials employing dual site-bond model

Ubaldo Gil Cruz*¹, Luis G. Bermudez Rodriguez¹, Israel Ibarra Solís¹, Isis Rodriguez Sanchez¹, Alonso Salazar Garibay¹

¹Instituto Politécnico Nacional (UPIIG). Av. Mineral de Valenciana No. 200 Col. Fracc. Industrial Puerto Interior, C.P. 36275 Silao de la Victoria, Guanajuato México.

Abstract:

Cylindrical-type porous materials such as MCM-41 and SBA-15 substrata have been the subject of intensive research. Nevertheless, a profound and unifying study concerning the effects of surface heterogeneity and networking effects are still lacking. This research aims to connect experimental results from adsorption data, specifically Pore-Size Distributions, with a theory describing porous space organization in terms of Pore-size heterogeneity and networking effects.

Keywords: Pore Distribution, DSBM, Site Pore, Bond Pore, Mesoporous, Molecular Dynamics, Fixed Network

I. Introduction

Synthesized porous materials have an important technological application as filters, membranes, catalysts, etc. [ref 1-3]. The last decade saw the birth of template synthesis with controlled sizes and shapes pore; one kind of these are the cylindrical-type solids such as the MCM-41 and SBA-15 materials [ref 4]. They have allowed evaluate different adsorption theories, such as: Density Functional, Monte Carlo and Molecular Dynamics [ref 5-9]

Also, No Local Density Functional Theory, NLDFT, have been a fundamental tool in the description of the fluid density confined to capillary filling, as is the case of gas adsorption inside pores with nanometer size. Then, NLDFT calculus has enabled the determination of the Pore-Size Distributions (PSD) for mesoporous materials [ref 10, 11].

Other computational methods have been employed for evidence on different mechanisms for filling and configuration of the fluids adsorbed inside of the pores. For instance; only through them was possible to know the process of the gas evaporation in ink-bottle type pore, it has been called cavitation [12-14]. Although, these theories and methods have allowed understanding the process of gas adsorption inside micro and mesoporous materials; they are limited to employ in models of the isolated pores with homogeneous shapes due to the high computational cost.

On the other hand, Dual Site-Bond Model (DSBM) have been used to describe gas adsorption on mesoporous materials [15]. This methodology has an advantage to decrease on time computational due to the simplicity models used to simulated the pores. Also, considered two types of porous: The sites and the bonds; a site pore is a cavity surrounded by necks pore which are communicated with neighboring by homologous cavities. While, a bond pore is a pore neck that connects two sites

(Figure 1a).

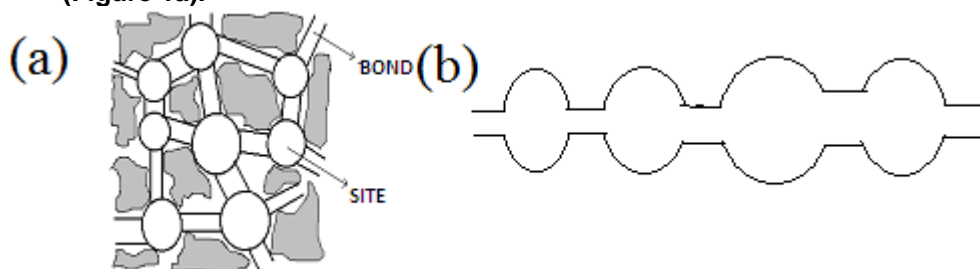


Figure 1. a) Pore models employed in DSBM b) pore model with connectivity of 2.

In DSBM, the pore phase is considered as spheres and cylinders interconnected throughout the void space. Also, it is necessary define the connectivity, C , which is the number of bonds emerging from a site; for example, a connectivity 2 considered one pore site and 2 bond pore as is shown in the Figure 1b. DSBM allowed calculated two pore distribution: $F_s(R_s)$ (site pore) and $F_b(R_b)$ (bond pore); then, the probability of finding pore site less to R_s and the probability of finding a bond pore smaller to R_b are calculate by Equation 1 and 2 respectively.

$$S(R_s) = \int_0^{R_s} F_s(R_s) dR_s \quad (1)$$

$$B(R_b) = \int_0^{R_b} F_b(R_b) dR_b \quad (2)$$

$S(R_s)$ and $B(R_b)$ are the area under the curve of pore distribution functions of element with $F_s(R_s)$, $F_b(R_b)$ sizes. Then, the construction of the pores with DSBM theory must comply with the construction rule (CP); which, suggest that a site pore is major to bond pore (Ec. 3). Also, a special correlation between site and bond pore given by Equation 4 should be considered in this model.

$$B(R) \geq S(R) \quad \forall R \quad (3)$$

$$\phi(R_s, R_b) = 0 \quad \forall R_s < R_b \quad (4)$$

The 3 and 4 equation allowed proposed a size correlation function: $\Phi(R_b, R_s)$ expressed by equation 5; where $B(R_b)$ and $S(R_s)$ are the probabilities of having a bond pore with size between 0 and R_b and a site pore with size between 0 and R_s , respectively.

$$\begin{aligned} \phi(R_s, R_b) &= \frac{\exp\left[-\int_{S(R_b)}^{S(R_s)} \frac{dS}{B-S}\right]}{B(R_s) - S(R_s)} \\ &= \frac{\exp\left[-\int_{B(R_b)}^{B(R_s)} \frac{dB}{B-S}\right]}{B(R_b) - S(R_b)} \end{aligned} \quad (5)$$

The aim of this work was to employed the DSBM theory to build the different pore model and simulate the pore distribution in a gas adsorption process. The connectivity was an important variable to consider in the model; a connectivity of the 2 was employed for all simulation. The pores distributions calculate by DSBM were compared with BJH distribution, an overlap between site and bonded pore were observed for some pore model builder.

II. Pore Models

Monte Carlo method was used to represent the solid pore space. Then, the first step was the fixed network that is still lacking. Subsequently, sites and bond pore were randomly assigned to obtained $F_s(R_s)$ and $F_b(R_b)$ distributions; which performed with the PC. Metropolis algorithm was employed to obtained the more optimum network until the equilibrium state. When, the equilibrium state was reached the function of correlation ($\Phi(R_b, R_s)$) took the shape corresponding to the equation (5) and the final porous network was constructed.

2.1 Methodology

Porous building networks using Monte Carlo methods may represent the pore space of a solid material [16]. Then the algorithm is detailed.

1. As a first step a fixed network with defined geometry: cubic, triangular, square, etc.
2. Subsequently randomly assigned to the sites and sizes of network links according to two distributions given $F_s(R_s)$ and $F_b(R_b)$, which comply with the PC.

3. Then through the Metropolis algorithm, the most plausible representation of the network is sought. This is achieved by allowing the network evolve through transitions that are consistent in size allowing exchange between two different sites, randomly chosen, or allowed the exchange the links between two different sizes, also chosen at random, towards the equilibrium state.

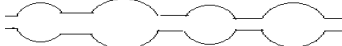


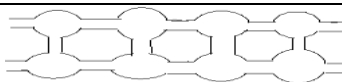
4. Finally, when this state of equilibrium is reached the function of correlation between all the links and neighboring sites took the shape corresponding to the equation (5). It is at this time ends the attempts to exchange links between sites and sizes and terminating the construction process of the porous network.

III. Results and Discussion

3.1 Simulation of Porous Networks

Several Porous networks were constructed according to Cordero et.al methodology; all networks consisted of 10^4 sites allocated at the nodes of a cubic lattice of constant side equal to 46. Table 1 shows the simulated condition used for the construction of the pore structures

Table 1. Statistical parameters of the simulated Porous Materials

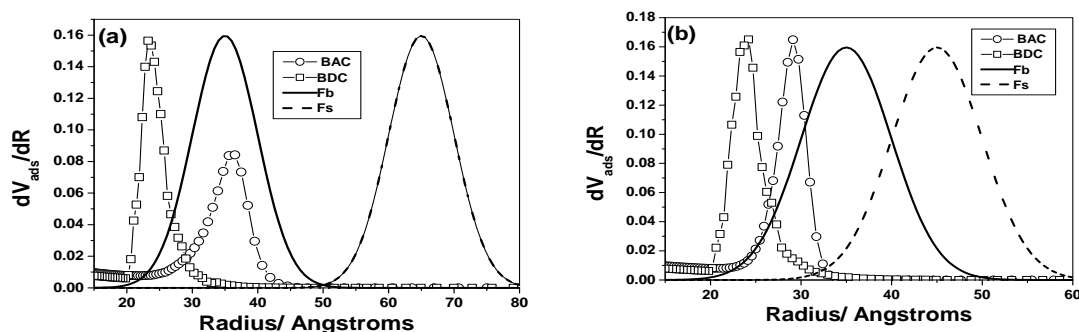
Material	$\bar{R}_B / \text{\AA}$	$\bar{R}_S / \text{\AA}$	Ω	$\sigma / \text{\AA}$	\bar{C}	Morphologies Models
I	35	65	0.0	5	2	
II	35	45	0.5	5	2	
III	35	38	0.9	5	2	
IV	55.5	57.5	0.9	6	2	

Networks I to III had a value of connectivity equal to 2; then, bond pores were chosen randomly and allocated at the x-axis of the network and the site pores were located at y-axis; while z-axis remained empty. The structures were visualized as a collection of heterogeneous and parallel tubes through the x-axis. Every tube had heterogeneous size; however, several cross-sectional areas were formed according to sites and bond pores interconnected.

Network IV had different morphology; sites and bonds pore were assigned to a cubic lattice, permitting all types of bonds pore at the x, y and z-axes. Then, several connectivity was used for the network, these change the $\frac{1}{2}$ to 2 at the end of the simulation process [17]. The final structure for IV network consisted in packages of the heterogeneous tubes interconnected with each.

3.2 Pore Distribution

Pore-Size Distributions were determined both at the Boundary Sorption Curves (Ascending and Descending) and at the set of the Primary Scanning Desorption Curves, for every network. BJH method with the Broekhoff-de Boer (BdB) equations were used to calculate the stability limit conditions of the adsorbed phase. It is worth noting to point out that a cylindrical geometry was assumed throughout the calculus of pore sizes. Some examples are; cylindrical interface for the adsorption curves and hemispherical meniscus for the desorption ones; the former in concordance with the fact that we studied cylindrical-type porous materials. The calculated sizes are shown in Figures 2 and 3.



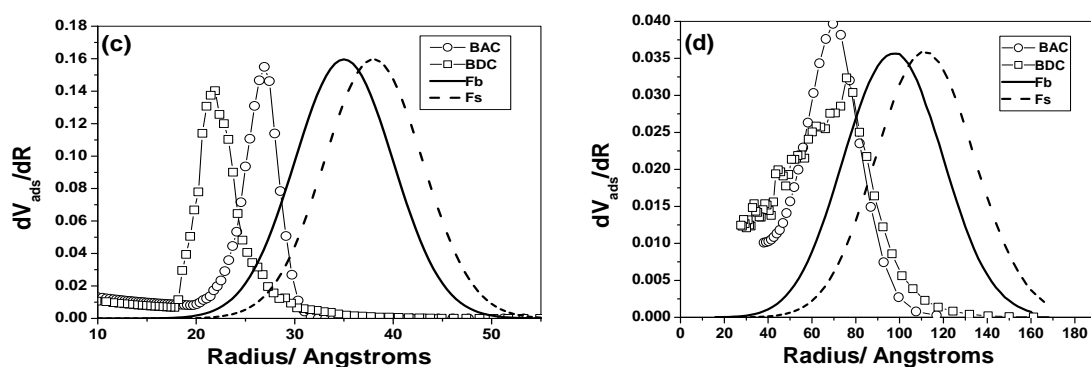


Figure 2. Pore-Size Distributions calculated at the Boundary Sorption Curve. (a) Network I; (b) Network II; (c) Network III; (d) Network IV.

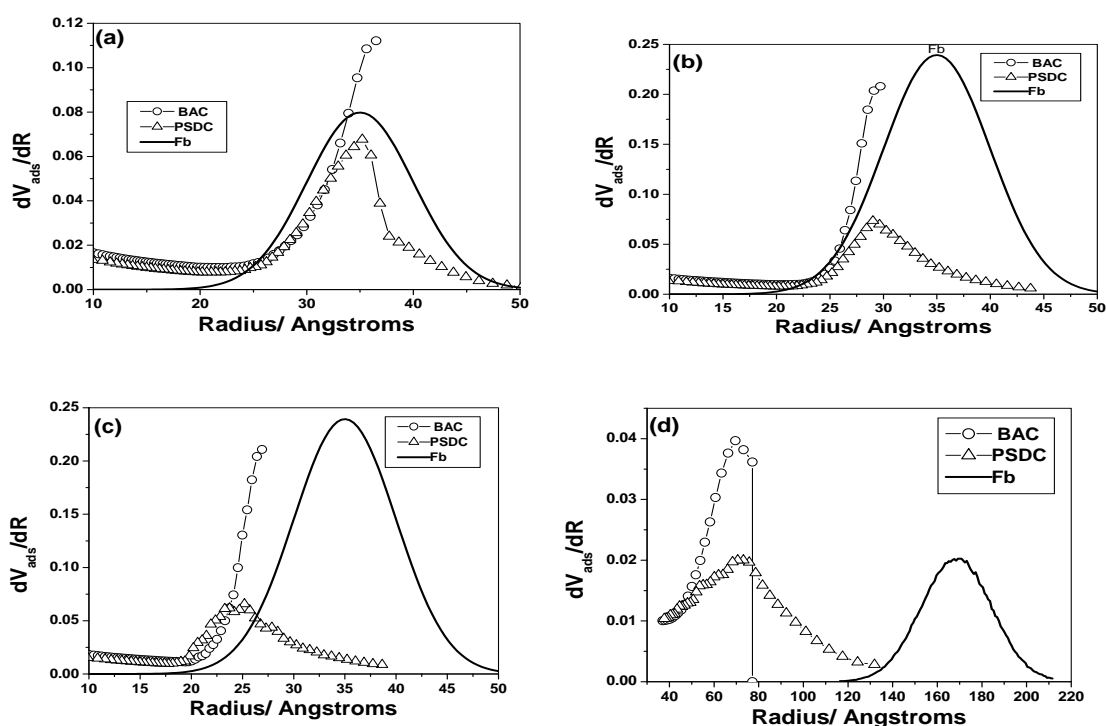


Figure 3. Pore-Size Distributions calculated at the Primary Scanning Desorption Curves. (a) Network I; (b) Network II; (c) Network III; (d) Network IV. Only one Scanning curve result is presented for every network.

According to Figure 2, pore models corresponding to III and IV network presented a more overlap between adsorption distributions calculated by DSBM; on the other hand, only network IV presented similar adsorption distribution between the calculated by DSBM and BJH model, these results suggested that this pore model should simulate better the pore distribution. However, desorption pore distribution was better simulate for network I and II, according to Figure 3, these pore models presented similar distribution between the graphic obtained by DSBM and BJH.

IV. Conclusion

DSBM models allowed simulate the pore networks employed for the description of the pore distribution of the mesoporous materials. When analyzing isotherms of SBA-15 and MCM 41 type materials, it is important to consider the effect of microscopic heterogeneities, which can show us the physicochemical effects that occur in these materials. Taking into account the size and therefore the pore geometry and the distribution of these, coupled with the connectivity and having overlapping distributions-linked site. It is something that can help us understand the different processes that take place and thereby determine the behavior of the hysteresis loop and the structure of the material being treated.

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