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Simulation of nitrogen sorption processes in materials with cylindrical mesopores: Hysteresis as a thermodynamic and connectivity phenomenon

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Abstract

A numerical simulation of nitrogen sorption in materials with cylindrical mesopores is proposed. Multilayer formation and capillary condensation–evaporation processes are followed by using the Sonwane and Bhatia's molecular-continuum model, although an empirical expression is used to represent the potential interaction between the adsorbate and the adsorbent. The pore structure of the solid is generated by inscribing 3D cylindrical pores in a 2D square lattice. The connectivity effects on the nitrogen isotherms are studied by using percolation theory. The ability to predict the multilayer thickness and the relative pressure at which phase transition takes place is corroborated with data reported in literature, finding good fittings in this work. On the other hand, we report for the first time a study on the effect that both pore mean diameter and connectivity have on the extent of hysteresis.

Keywords: Adsorption isotherm; Connectivity; Capillary condensation; Simulation; Hysteresis; Percolation

1. Introduction

Nitrogen adsorption is the most used instrumental technique for characterization of the porous structure of different kinds of materials. By this technique it is possible to find pore size $\langle d \rangle$, pore volume (V_p), pore size distribution (PSD) and total surface area (S_t). As it has been well established (Gregg and Sing, 1982), the adsorption process in mesopores involves the formation of an increasing thickness film, followed by capillary condensation. Since the Kelvin's model was proposed in 1871, it has continuously been used to find the thermodynamic stability limit of the film thickness, in which capillary condensation takes place (Sing, 1998). Traditional methods to calculate PSD, such as the one developed by Barret, Joyner and Halenda (BJH) (Barrett et al., 1951), are based in this theory. However, the Kelvin's theory does not take into account the interface curvature and the adsorbate–adsorbent interaction potential effect on the chemical potential of the adsorbed film (μ_a). Different empirical equations, which try to predict film thickness (t) as a function of gas pressure, have been developed. In 1967, Broekhoff and deBoer (BdB) (Broekhoff and De Boer, 1967), proposed a thermodynamic model, which relates the thickness and the chemical potential of the film by a function that represents the adsorbate–adsorbent potential ($F(t)$). In this treatment, $F(t)$ is independent of pore size and the curvature effect on the surface tension is again neglected. The validity of these theories had not been proven, due to the absence of solids with non-connected uniform pores that served as a model for this study. Such a scenario changed radically in 1992 with the MCM-41 materials synthesis (Beck et al., 1992). Now, it is well recognized that the Kelvin's equation has significant deviations when predicts capillary condensation and therefore leads to an underestimation of the real pore size when BJH's model is used. Moreover, the use of BdB's equation can be justified only when there are pore sizes larger than 100 Å. Many efforts have recently been done by theoreticians and experimentalists for predicting, in a more exact way, the multilayer formation as well as the pressure at which the capillary condensation or evaporation occurs. With this purpose, new models or

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modifications to the BdB's model have been stated (Neimark and Ravikovitch, 2001; Qiao et al., 2003; Sonwane and Bhatia, 1998a, b, 1999; Zhu et al., 1998, 1999). By taking into consideration the curvature effect on the surface tension and the pore geometry and by using an adsorbate–adsorbent interaction potential,which depends on the radius (r), Sonwane and Bhatia (1998a) introduced a continuous molecular model that describes satisfactorily the capillary coexistence curves in MCM-41 materials. However, the proposed adsorbate–adsorbent potential function, is a complex expression, that it is not easy to be used in routine analysis (Qiao et al., 2003) and new empirical expressions to represent this potential have been proposed (Qiao et al., 2003; Zhu et al., 1998). It is important to emphasize that in these works, a single pore is used and therefore the results show deviations when PSD increases. Moreover, these models failed predicting different hysteretical behaviors in materials with interconnected pores, where the connectivity effect becomes important.

Studies that relate connectivity and extent of hysteresis, in the frame of a percolation-type phenomenology, can be found in the literature (Liu et al., 1992; Neimark, 1991; Seaton, 1991). Most of these works deal with a single percolating cluster spanning the lattice, without taking into account the network configurations involving pores cluster distributions below and above the percolation threshold. Recently, Ramírez et al. (2005) showed it was possible to have hysteresis even under this threshold.

In this work, a numerical simulation of the nitrogen sorption processes in interconnected cylindrical mesopores is shown. The adsorbed film thickness is calculated according to the BdB's theory, but considering the curvature and pore size effect on the surface tension and the adsorbate–adsorbent interaction potential, respectively, as it has been suggested by Sonwane and Bhatia (1998a). An empirical expression to represent such interaction is proposed. The coefficients in this expression are fitted until the film thickness is reproduced as a function of pore diameter and relative pressure according to Sonwane and Bhatia (1998a). The limits of thermodynamic stability, where capillary condensation or evaporation occurs, are also calculated. The ability to predict the film thickness and the relative pressure at which phase transition takes place, is corroborated with reported experimental data (Kruk et al., 2000a). Unlike other recent reported works, which try to predict isotherms based upon a single pore (Neimark and Ravikovitch, 2001; Qiao et al., 2003; Sonwane and Bhatia, 1998a, b, 1999; Zhu et al., 1998, 1999), the adsorption is given in an interconnected mesoporous network, representing our solid. Here the pore connectivity (n) and PSD can be modulated. This is the first published study on the effect that the connectivity and pore diameter have on the following two parameters: (a) hysteresis area (A_h) and particularly (b) normalized hysteresis area at V_0 (A'_h) (V_0 is the maximum volume of N_2 adsorbed by the porous sample). Each effect is separately studied, with the isotherms simulated assuming a single pore size or an evaporation and capillary condensation occurring at the same relative pressure for the same kind of pore. Finally, the synergistic effect of connectivity and pore diameter on these parameters is studied.

2. Model

2.1. Sample construction

Our solid is generated by occupying randomly a fraction (p) of the sites that constitute a square lattice, and inscribing cylindrical pores between two neighbor sites (Ramírez et al., 2005). A new porous structure can easily be obtained, by changing the seed of the random number generator (William, 1991). Up to five different pore configurations are simulated for each p-value in order to obtain configurational averages. The pore diameter is assigned randomly, following a Gaussian distribution:

$$N_p(d_p) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\left(\frac{d_p - \langle d\rangle}{\sqrt{2}\sigma}\right)^2\right), \tag{1}$$

where $N_p(d_p)$ is the number of pores with diameter d_p, whereas $\langle d\rangle$ (Å) represents the pore mean diameter and σ (Å) is the standard deviation of the distribution. We have assumed a pore length equal to the diameter as it has been described elsewhere (Loh and Wang, 1995; Meyers and Liapis, 1998; Meyers et al., 2001). We have developed a new algorithm for cluster labeling in a consecutive fashion, with which is likely to have an effective control of all pores in the network (Ramírez et al., 2005). Internal pores clusters are not available for invasion. For this reason, they are not taken into account for both the connectivity and adsorbed volume calculations. Average connectivity $\langle n\rangle$ per pore available for invasion reads as follows:

$$\langle n\rangle = \frac{1}{N_i N} \sum_{k=1}^{N} \sum_{\langle i,j\rangle} z(i,j), \tag{2}$$

where N_i is the number of pores available for invasion, N is the number of different pore configurations or number of samples, the second sum runs over the nearest pores and $z(i,j)$ is the coordination number for a (i,j) pore (Ramírez et al., 2005).

2.2. Film thickness and capillarity

According to Sonwane and Bhatia, the adsorbed film thickness t (Å) on the internal wall of each pore, can be calculated for adsorption or desorption, respectively, as follows:

$$\frac{\mathrm{d}(\Delta G)}{\mathrm{d}N} = \int_{P_g}^{P_0} V_g\,\mathrm{d}P + \phi(t,r) - \frac{V_L\gamma_\infty(r-t)}{(r-t-(\lambda/2))^2} = 0, \tag{3}$$

$$\frac{\mathrm{d}(\Delta G)}{\mathrm{d}N} = \int_{P_g}^{P_0} V_g\,\mathrm{d}P + \phi(t,r) - \frac{2V_L\gamma_\infty(r-t)^2}{[(r-t)(r-t-\lambda)+\lambda\sigma_{ff}/4](r-t-\lambda)} = 0. \tag{4}$$

Here ΔG is the change in free energy for the adsorption process, V_g is the molar volume of the gas, γ_∞ is the vapor–condensate surface tension (8.88×10^{-3} N/m), V_L is the molar volume of the adsorbed interface (34.68 cm^3/gmol), r is the pore radius, σ_{ff} is the intermolecular interaction adsorbate–adsorbate parameter (3.681 Å), λ is the interlaying spacing of the fluid