# Pore Size Distribution Analysis of Selected Hexagonal **Mesoporous Silicas by Grand Canonical Monte Carlo** Simulations

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Received April 12, 2005. In Final Form: July 13, 2005

We combine here a regularization procedure with individual adsorption isotherms obtained from grand canonical Monte Carlo simulations in order to obtain reliable pore size distributions. The methodology is applied to two hexagonal high-ordered silica materials: SBA-15 and PHTS, synthesized in our laboratory. Feasible pore size distributions are calculated through an adaptable procedure of deconvolution over the adsorption integral equation, with two necessary inputs: the experimental adsorption data and individual adsorption isotherms, assuming the validity of the independent pore model. The application of the deconvolution procedure implies an adequate grid size evaluation (i.e., numbers of pores and relative pressures to be considered for the inversion, or kernel size), the fulfillment of the discret Picard condition, and the appropriate choice of the regularization parameter (L-curve criteria). Assuming cylindrical geometry for both porous materials, the same set of individual adsorption isotherms generated from molecular simulations can be used to construct the kernel to obtain the PSD of SBA-15 and PHTS. The PSD robustness is measured imposing random errors over the experimental data. Excellent agreement is found between the calculated and the experimental global adsorption isotherms for both materials. Molecular simulations provide new insights into the studied systems, pointing out the need of high-resolution isotherms to describe the presence of complementary microporosity in these materials.

#### I. Introduction

The demand from the industrial sector of large poresize adsorbents with well-defined geometry endorsed the inception of the well-known family of mesoporous molecular sieves M41S. One of the highlighted members is the hexagonally ordered MCM-41, coined by Mobil Corporation in the early 90's.<sup>1</sup> MCM-41 was manufactured under conditions where silica-surfactant self-assembly occurred simultaneously with condensation of the inorganic species, yielding mesoscopically ordered composites. The research evolution was driven to the extension of surfactant-template procedures, to include a wide range of compositions, and to explore different structuredirecting functions, establishing the aim of several theoretical and experimental studies.<sup>2-8</sup> For this purpose,

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nonionic block copolymers, an interesting class of structuredirecting agents whose self-assembly characteristics lead to kinetically guenched structures, were used on those synthesis. Block copolymers have the advantage over surfactants that their ordering properties can be nearly continuously tuned by adjusting solvent composition, molecular weight, or copolymer architecture.

Nowadays, the next generation of hexagonal mesoporous materials such as SBA-15 (Santa Barbara-x)<sup>9</sup> and PHTS (Plugged hexagonal templated silica)<sup>10</sup> have attracted much interest on both science and technology fields, due to their potential applications in shape-selective catalysis, separation of large molecules, purification of fluids, fabrication of membranes, and also as directing patterns for other materials. SBA-15 high ordered mesoporous silica exhibits a remarkable hydrothermal stability<sup>11</sup> compared to MCM-41 and can be synthesized in a wide range of pore sizes and particle morphologies. SBA-15 has already been tested for several applications in the fields of catalysis, separations, and advanced optical materials.<sup>11-17</sup> The

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PHTS belongs to the SBA-15 family of materials, with the particularity that, depending on the synthesis conditions, some silica is deposited inside the pores, plugging them.<sup>10</sup> This provides the material with unprecedented thermal, hydrothermal, and mechanical stability.

Published works related to the experimental characterization of SBA-15 are those done by Ryoo et al.<sup>18</sup> and Kruk et al.<sup>19,20</sup> Kruk et al.<sup>19</sup> synthesized SBA-15 following the procedure described by Zhao et al.<sup>9</sup> and then performed a systematic study of the structure of this material by means of X-ray diffraction, thermogravimetric analysis, and nitrogen adsorption; the mesopore size distribution was calculated on the basis of adsorption branches of nitrogen isotherms using the BJH method with the corrected form of the Kelvin equation. They provided supported explanations for the existence of the complementary porosity arranged in a mesopore-micropore network as a result of the properties of the triblock copolymer templates.<sup>19,20</sup> Additionally, they proposed an explanation of a plug formation mechanism that leads to the synthesis of PHTS adsorbents.<sup>20</sup>

The objective of the present work is to tune a methodology for the determination of PSDs of SBA-15 and PHTS in a synergetic manner, by combining nitrogen adsorption data and grand canonical Monte Carlo (GCMC) simulations with a regularization method. We make special emphasis on the robustness of the obtained PSD, using different physical and mathematical arguments to support the final proposed PSD. The work presented here is part of an ongoing project toward the development of a reliable methodology for PSD analysis based on adsorption data combined with statistical mechanics tools.<sup>21-24</sup> In fact, the development of reliable methods for the accurate characterization of porous materials remains an on-top and motivating problem now-a-days,<sup>25,26</sup> especially for materials with a wide range of pore sizes and shapes and for heterogeneous surface materials. Research is focused on two main topics, both related to obtain the PSD from inversion of the adsorption integral equation: a reliable method to obtain the kernel of individual adsorption isotherms, and a robust mathematical procedure to invert the integral. Statistical mechanics provides two approaches to obtain the individual adsorption isotherms: the density functional theory (DFT) and molecular simulations (MS). Progress in molecular modeling of adsorption phenomena by means of DFT calculations and MS has led to a better understanding of the specific interactions of adsorbed species with porous material.<sup>23,27–38</sup> However, in some of these works, some limitations of the methodology for the determination of the PSD could have been screened either by intrinsic

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drawbacks in the material selection such as high tortousity, effective surface area far away from individual pore model applicable conditions (e.g., activated carbon, controlled pore glasses, and some others), by approximations made in the applied theories, and/or by ignoring relevant energetic heterogeneities. A way to isolate the impact of each assumption is by first applying the methodology to materials with well-defined geometry and morphology. In this case, deviations would come either from the method used to model the individual adsorption isotherms (DFT or MS), which can be refined by direct comparison with the experimental data, or by ignoring the connection among the pores. If the methodology is applied to porous materials with well-defined geometry and unconnected pores, the only assumption to be validated is the adsorption behavior in individual pores, in addition to the mathematical procedure to invert the adsorption integral.<sup>24</sup>

Within this framework, we have developed a protocol to obtain robust PSD of adsorbent materials by combining GCMC simulations with a regularization procedure and experimental data. As a first step in checking the reliability of the procedure for the characterization of materials, the method was applied with success to selected MCM-41 materials, chosen for their well-defined pore geometry (cylindrical) and unconnected pores.<sup>25</sup> The methodology is applied here as the following step to SBA-15 and PHTS. These materials are excellent candidates to check the developed methodology for PSD analysis: they have welldefined cylindrical mesopores with a narrow PSD, measurable from other experimental techniques; they also present a microporous region which can be explored with these types of theoretical methods. In these materials, the pores have a defined geometry, but they are connected. Ravikovitch and Neimark<sup>27</sup> were the first ones who characterized these materials with the DFT approach. They used nitrogen adsorption isotherms on SBA-15 materials prepared in different research groups, and applied a method for the characterization of SBA-15 based on nonlocal (NL) DFT, assuming cylindrical geometry. They just determined the size distribution of the main channels and the amount of the intrawall porosity, without characterizing the microporous region. The structural parameters obtained were in excellent agreement with previous described geometrical considerations and X-ray diffraction data. However, as pointed out by the authors, one of the shortcomings of their NLDFT model is that the

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calculated global adsorption isotherm exhibited pronounced layering [see Figure 4 of ref 27], as a consequence of the layering transitions observed in some individual pores [Figures 2 and 3 of ref 27]. They argued that this layering was an artifact caused by the use of the simplified, structureless pore wall model and/or approximations made in the DFT theory. Since in the present work we use MS instead of DFT to model the same materials, we will try to answer this question raised by the authors.

The rest of the paper is organized as follows. In the next section, we briefly present the experimental and modeling methodology used, including details on the synthesis of the materials, the application of the regularization procedure, and the molecular simulations. The main results related to the structural characterization of the synthesized materials, GCMC simulations, and the robustness of the regularization procedure are presented and discussed in section III. Finally, we summarize the main conclusions from this work in section IV.

## **II. Methodology**

Although the main purpose of the present work is to test the characterization methodology, and hence, available experimental data could be used, we have decided to synthesize the materials under study in our laboratory. Our final goal is to use the combined experimentalmodeling procedure for further applications of these materials, and hence, we would like to control the whole cycle: experimental synthesis and characterization, model tuning by comparison with the experimental data, predictions from the model for further applications of the selected material, and validation of the predictions.

**II.1. Experimental Section.** Two materials with distinct structural characteristics were synthesized in our laboratory, SBA-15 and PHTS. In a typical synthesis, 4.0 g of Pluronic P123 were dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35 °C. Then 8.5 g of TEOS was added into that solution stirring at 35 °C during 20 h for SBA-15 (5 h for PHTS). Each mixture was aged at 80 °C overnight without stirring. The white solids were filtered, washed, and slowly burned, increasing from room temperature up to 500 °C in 8 h, remaining at 500 °C for 6 h.

Porosity and surface area analysis were performed on an ASAP 2010 V4.00 automated gas adsorption system (Micromeritics Instrument Corporation). The burned samples were degassed for 17 h at 200 °C. Gas adsorption was measured using nitrogen as the adsorbate at liquidnitrogen temperature.

The PHTS material was synthesized changing the stirring time proposed by Zhao et al. for SBA-x;<sup>9</sup> we have used 5 h instead of 20 h. The obtained material is fully comparable with the material PHTS-3 described by Van Der Voort et al.<sup>10</sup> In fact, in the procedure described by Van Der Voort et al., the variation of the surfactant/TEOS ratio, synthesis temperature, and time ended with different PHTS-x materials. We have observed that the stirring time also provides a parameter to tune the properties of the synthesized PHTS materials.

**II.2. Molecular Model.** To mimic the adsorption behavior on selected materials, we have assumed the validity of the independent pore model:<sup>35</sup> the global adsorption behavior of the material is due to the contribution of the individual pores with different diameters integrating the material, ignoring the connectivity among them. This maybe a problem for tortuous, interconnected porous materials, but it has proved to be accurate for MCM-41 materials.<sup>25</sup> It also seems a reasonable assumption for

SBA-15 and PHTS: they present two main pore ranges, one with a broad distribution of micropores and another more relevant for further applications, corresponding to a narrow mesopores distribution with a well-defined pore size. Hence, we modeled the global adsorption of the materials in terms of several individual adsorption isotherms, obtained by GCMC simulations at different pressures and pore sizes.

The fluid-fluid interactions were modeled as single Lennard-Jones (LJ) spheres, with nitrogen parameters  $\sigma_{\rm ff} = 0.3615$  nm and  $\epsilon_{\rm ff}/k = 101.5$  K, k being Boltzmann's constant. Those fluid-fluid parameters were chosen by Ravikovitch et al.<sup>38</sup> to fit with bulk properties of the adsorbate, including liquid-gas surface tension and reference adsorption isotherms on nonporous substrates.

SBA-15 and PHTS were modeled as a collection of individual pores, assumed to be infinite cylinders with silica walls. The silica–gas interactions on such pores were modeled as the LJ interactions with an integrated smooth cylindrical layer of oxygen atoms. The structureless potential of the solid-fluid interaction used in this work is given by<sup>39</sup>

$$\begin{split} \phi_{\text{wall}}(r,\!R) &= \pi^2 \rho_{\text{s}} \epsilon_{\text{sf}} \sigma_{\text{sf}}^{-2} \! \left[ \frac{63}{32} \! \left[ \frac{r}{\sigma_{\text{sf}}} \! \left( 2 - \frac{r}{R} \right) \right]^{-10} \times \\ F \! \left[ -\frac{9}{2} \! , \! - \frac{9}{2} \! ; \! 1 \! ; \! \left( 1 - \frac{r}{R} \right)^2 \right] - 3 \! \left[ \frac{r}{\sigma_{\text{sf}}} \! \left( 2 - \frac{r}{R} \right) \right]^{-4} \times \\ F \! \left[ -\frac{3}{2} \! , \! - \frac{3}{2} \! ; \! 1 \! ; \! \left( 1 - \frac{r}{R} \right)^2 \right] \end{split}$$
(1)

where the product  $\rho_s \epsilon_{sf}/k = 22.5369$  K Å<sup>-2</sup>, where  $\rho_s = 0.153$ Å<sup>-2</sup> is the effective surface number density of the oxygen atoms in the pore wall,  $\epsilon_{sf}/k = 147.3$  K is the LJ energy parameter between the solid and the fluid, and the combined molecular size solid–fluid parameter  $\sigma_{sf} = 0.317$  nm. Those parameters were selected for comparative purposes with the previous work done in the system SBA-15/nitrogen by Ravikovitch et al.,<sup>27</sup>  $F[\alpha,\beta,\gamma,\chi]$  are the hypergeometric functions.<sup>40</sup> The wall potential was calculated at a given distance r (in the radial direction) when the radius of the pore is R.

**II.3. Simulation Conditions.** We have obtained the individual adsorption isotherms by GCMC simulations. In GCMC, the temperature, T, the volume pore, V, and the chemical potential,  $\mu$ , are kept fixed. The number of molecules is thus allowed to vary, and its average is the relevant quantity of interest. For convenience, to obtain the adsorption isotherm, we ran simulations at different values of the activity,<sup>41</sup>  $\xi$ , defined as

$$\xi = \frac{\exp(\mu/kT)}{\Lambda^3} \tag{2}$$

where  $\Lambda$  is the de Broglie wavelength, which includes contributions from translational degrees of freedom, and  $\mu$ , k, and T were defined previously.

The usual magnitudes for representing adsorption data are the amount adsorbed in the pore versus the relative pressure  $p/p_0$  in the bulk phase; here  $p_0$  is the bulk saturation pressure. The activity is related to the pressure by  $((p/p_0) = (\xi/\xi_0))$ , which implies that the bulk phase in

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thermodynamic equilibrium with the pore presents an ideal behavior. We have checked that the corrections for the gas-phase nonideality were small, usually less than 10% in the value of  $p/p_0$ . The chosen state point for reduction of activities to pressures was the saturation point of pure nitrogen at 77 K, found to occur at  $\xi_0 =$ 0.0823 nm<sup>-3</sup>. This result was calculated through a suitable equation of state, the soft-SAFT equation,<sup>42,43</sup> using the nitrogen LJ parameters described above at needed conditions.

Almost all simulation runs required  $2.5 imes 10^8$  configurations to reach the equilibrium. Additional 5 imes 10<sup>8</sup> configurations were generated for average purposes. At some conditions, longer runs were needed to accomplish the equilibrium conditions. Average properties were calculated over blocks with 5  $\times$  10  $^{5}$  configurations. The fluid-fluid potential was cut at  $r_{\rm c} = 5\sigma_{\rm ff}$  and no long range corrections were added. For a detailed discussion on the issue of the cutoff length and the addition of long range corrections in simulations of inhomogeneous fluids, the reader is referred to ref 44.

To compare with experimental data, the excess pore fluid density was calculated as

$$\langle \rho_{\rm exc} \rangle = \frac{\langle N \rangle}{V} - \rho_{\rm bulk}$$
 (3)

where  $\langle N \rangle$  is the mean number of particles inside the pore,  $\rho_{\text{bulk}}$  is the bulk density value at the same conditions, calculated from soft-SAFT,  $^{42,43}$  and V is the volume of the model pore.

II.4. Regularization Procedure. The calculation of the PSD of porous materials from adsorption data has been addressed by several authors, <sup>19,20,23,24,27,45,46</sup> using a variety of different available approaches. However, to our knowledge, not a detailed study has been published on the influence of some key variables, such as the kernel size, the inversion procedure, the robustness of the obtained PSD versus errors in the experimental data, etc, on the final PSD. These questions will be addressed in some detail here.

We have chosen to use Tikhonov's regularization method through a singular value decomposition (SVD) as we consider it to be most adequate for PSD analysis purposes: (1) it is simple to implement, (2) it is very fast, as it is a direct (as opposed to iterative) method, and (3) it is one of the best mathematically founded methods for that purpose. Hence, we focus here on the mathematical details of the adaptable procedure of deconvolution over the adsorption integral equation followed in this work. The deconvolution procedure implies a grid size evaluation, i.e., to select the number of pores and relative pressures to be included in the analysis, in addition to the adequate choice of the regularization parameter.

To obtain the PSD, f(D), the adsorption integral equation should be inverted

$$a_{\rm e}(P) = \int_{D_{\rm min}}^{D_{\rm max}} A_{\rm s}(P,D) f(D) \,\mathrm{d}D \tag{4}$$

where  $a_e(P)$  is the experimental adsorption isotherm at pressure P,  $A_s(P,D)$  gives the single-pore adsorption isotherm for each pore-size D (in the range  $D_{\min} - D_{\max}$ ), and it is the so-called kernel of the integral equation.<sup>47</sup>

This problem is tantamount to that of solving a Fredholm integral equation of the first kind. As it is well-known, this is an ill-posed problem, in the sense that the mapping  $a_e \rightarrow f$ , given by eq 4, is undefined because either the mapping is not continuous or the image *f* is not unique. From a practical point of view, the lack of continuity implies that f is highly sensitive to arbitrary small perturbations in the experimental data  $a_{\rm e}$ . This poses a first problem of reproducibility of any solution to eq 4, and thus the problem, as stated before, has physically (and mathematically) no sense. Standard approaches<sup>47</sup> to this problem rely on solving the related problem of finding the solution f that minimizes the functional

$$J[f] \equiv ||a_{e}(P) - \int_{D_{\min}}^{D_{\max}} A_{s}(P,D) f(D) dD||^{2} + \lambda^{2} ||\int_{D_{\min}}^{D_{\max}} R(D',D) f(D) dD||^{2}$$
(5)

where || || denotes an appropriate defined norm and  $\lambda$  is the so-called regularization parameter. The additional term renders the former problem into a well-defined one for each pair  $\lambda$  and R(D',D) and corresponds to the Tikhonov's regularization method.

In our case, only a finite set of experimental data or simulations results are available. Thus, eq 4 becomes a system of linear equations  $\mathbf{a}_{e} = \mathbf{A}_{s} \mathbf{x}$ , where  $\mathbf{A}_{s}$  is a matrix of single-pore adsorption isotherms (m pressures  $\times n$ pores). Here,  $x_i = f(D_i)\Delta D_i$ , where  $\Delta D_i$  is the pore-size interval associated to the pore size  $D_i$  after discretizing eq 4. The corresponding regularized problem can be recast as

$$\min_{\mathbf{x}} \{ ||\mathbf{a}_{e} = \mathbf{A}_{s} \mathbf{x}||_{2}^{2} + \lambda^{2} ||\mathbf{R} \mathbf{x}||_{2}^{2} \}$$
(6)

Although appropriate choices of the regularization term R may improve convergence to the unregularized solution,<sup>48</sup> we will consider the simplest case of  $\mathbf{R} = \mathbf{I}$  (the Identity matrix). The solution can then be obtained through a singular value decomposition of the matrix A<sub>s</sub>  $=\sum_{i=1}^{n}s_{i}\mathbf{u}_{i}\mathbf{v}_{i}^{\mathrm{T}}$ 

$$x_{\lambda} = \sum_{i} \frac{s_i^2}{s_i^2 + \lambda^2} \frac{\mathbf{u}_i^{\mathrm{T}} a_{\mathrm{e}}}{s_i} \mathbf{v}_i \tag{7}$$

where  $s_i$  is the set of singular values of  $\mathbf{A}_s$  that decay monotonically  $s_1 \ge s_2 \ge ... \ge s_n \ge 0$  (assuming  $m \ge n$ ), and  $\mathbf{u}_i$  and  $\mathbf{v}_i$  are the left and right singular vectors, respectively.

The SVD method requires the experimental data and the obtained kernel to fulfill a mutual suitability criterion given by the discrete Picard condition (DPC).49 This condition determines the convergence of *f* to the unregularized solution as well as the similarity between different solutions. The DPC requires that the Fourier coefficients  $|\mathbf{u}_i^{\mathrm{T}}\mathbf{a}_{\mathrm{e}}|$  decay faster than  $s_i$  on average. The mathematical formulation is that the values  $r_i$  defined as

$$r_{i} \equiv s_{i}^{-1} (\prod_{j=i-q}^{j=i+q} ||\mathbf{u}_{i}^{\mathrm{T}}\mathbf{a}_{\mathrm{e}}||)^{1/(2q+1)}$$
(8)

should decay monotonically within some range of the high

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 $s_i$ . Here q is a small integer that determines the amount of averaging. Appropriate vales for q are 1, 2, or 3.

An adequate method for the selection of  $\lambda$  must also be specified. There are different available methods which are not completely equivalent. The selection may depend on the specific problem. One such method is the (generalized) discrepancy principle,<sup>47,48</sup> which relies on having information of the experimental data error. The value of the regularization parameter is then chosen such that the residual norm  $||\mathbf{a}_{e} - \mathbf{A}_{s}\mathbf{x}||_{2}$  equals that error. Other methods rely on the particular mathematical properties of each selection scheme, e.g., the so-called L-curve. The latter is obtained by plotting the regularization term ||Rx|| versus the residual norm  $||\mathbf{a}_{e} - \mathbf{A}_{s}\mathbf{x}||_{2}$  for different values of  $\lambda$ , thus obtaining a curve which mainly consists of two branches forming an "L". The corner of this curve provides a mathematically sound criterion for choosing the value of  $\lambda^{48}$ . The basic criterion for any of these approaches is the condition that a good regularization parameter should yield a fair balance between the regularization term and the residual norm. Indeed, from the above discussion, we shall expect to have  $0 < ||\mathbf{a}_e - \mathbf{A}_s \mathbf{x}||_2$  within the experimental errors.

Although this formulation of the problem is mathematically sound, we still face many ambiguities from a physical point of view. First of all, we have the very stringent condition f(D) to be a nonnegative function (feasibility condition). Second, we aim at finding a systematic and robust procedure to determine a feasible solution. This means not only the obvious idea of robustness against errors in the experimental data and molecular simulations, which the regularization procedure already provides. We shall also require robustness against the very selection of the experimental data and the kernel to be used. In addition, this selection may affect the usual robustness against errors in the data. Thus, this raises the additional ambiguity of choosing a set of input data, as different sets show different robustness. In other words, different sets of experimental data and kernel should yield similar enough PSDs and either a similar or an optimized robustness against errors in the input data. Hence, a complete systematic procedure shall give a prescription for choosing a sound set of experimental data and the kernel to be used. Common mathematical procedures, like the one we use, are not guaranteed to either satisfy or completely answer these requirements. Therefore, to obtain a reliable solution, further inspection of the given data is needed.

Guided by these ideas and considering the additional requirement of nonnegativity of the solution  $\mathbf{f}_{\lambda}^{k} > 0$ , we have chosen  $\lambda$  as the smallest value for which this requirement is fulfilled  $\lambda_{\text{feas}}$ , i.e., the smallest  $\lambda$  for which a feasible solution is obtained. Note that since  $\mathbf{v}_i$  changes sign more often as  $s_i$  decreases,  $f_0$  becomes in general an unfeasible solution. We shall also require this value to lie close to the corner of the L-curve. The implicit assumption here is that the L-curve varies smoothly with the Lagrange parameter  $\mu^2$  corresponding to the additional feasibility constraint. Indeed the obtained values would lie close to the corner of the actual L-curve. Some preliminary results on this line were presented in ref 24, where some additional tests, besides the mathematical requirements outlined above, were pointed out. A throughout study on the applications of these requirements to two materials is presented here.

## **III. Results and Discussion**

We first present the experimental characterization of the synthesized materials PHTS and SBA-15 in terms of



**Figure 1.** Experimental nitrogen (at 77 K) adsorptiondesorption isotherms for PHTS (a) and SBA-15 (b). The solid line is a guide to the eye.

experimental nitrogen adsorption isotherms, followed by some selected individual adsorption isotherms for these materials generated by GCMC simulations. The experimental and simulated adsorption isotherms were used to check the convergence solution of the PSD analysis, using the DPC and the L-curve criteria, over five different kernel sizes in the PHTS material. We show here the effect of increasing the number of pores keeping constant the pressure points (for the PHTS material) and the effect of increasing the pressure values for a given number of pores (for the SBA-15 material). An additional test to check the robustness of the calculated PSD has been performed by adding random errors into the experimental data in both cases.

To perform a fair comparison between experimental and simulated results, it is important to note that the experimental adsorption isotherm represents the amount of fluid adsorbed per unit of mass of the solid, whereas the simulated adsorption isotherm represents the amount of adsorbed fluid per unit of void volume. These two concepts of volume are related by the true density and the porosity of the material. We have used the value of the true density as 2.2 g/cm<sup>3</sup> for pure silica. The porosity has been calculated by a trial and error procedure, checking that  $\mathscr{D} f(D) dD = 1$ , where  $\mathscr{D}$  represents the porosity and f(D)is expressed in  $(\text{length})^{-1}$  units.

Figure 1 shows the experimental adsorption/desorption nitrogen isotherms at 77 K in PHTS and SBA-15. PHTS textural characterization results can be seen in Figure 1a, where the adsorption/desorption nitrogen isotherms at 77 K show the form of a material coined by Van Der Voort et al. as PHTS-3.<sup>10</sup> This isotherm exhibits a



**Figure 2.** Individual nitrogen adsorption isotherm for silica-based materials obtained by GCMC.  $D = 1.5 \text{ nm}(\bullet)$ ,  $D = 3.0 \text{ nm}(\bullet)$ ,  $D = 4.5 \text{ nm}(\blacksquare)$ ,  $D = 6.0 \text{ nm}(\bullet)$ ,  $D = 7.5 \text{ nm}(\blacktriangle)$ , and D = 14 nm (triangle left solid). The figure on the left is a closeup of the low-pressure region, whereas the figure on the right shows the complete adsorption isotherm for each individual pore.

hysteresis loop type E following the de Boer classification.<sup>50</sup> corresponding to type H2 according to the IUPAC classification.<sup>26</sup> Type H2 hysteresis loops may be produced by tubular pores that contain a narrow constriction or closed pores of the inkbottle type.<sup>50</sup> The as-synthesized PHTS has an average pore diameter (4V/A by BET) of 34.4 Å, a pore volume of 0.575 cm<sup>3</sup>/g, and a BET surface area of  $666 \text{ m}^2$ /g. The BJH adsorption average pore diameter (4V/ A) is 40.5 Å.

The isotherm shown in Figure 1b is typical for the SBA-15 material,<sup>9</sup> exhibiting a well-defined hysteresis loop type A, following the de Boer classification,<sup>50</sup> corresponding to a type H1 hysteresis loop according to the IUPAC classification.<sup>26</sup> Type H1 hysteresis loops have been associated with capillary condensation and desorption in open-ended cylindrical mesoporous.<sup>51,52</sup> The synthesized SBA-15 material has an average pore diameter (4V/A by BET) of 41.9 Å, a pore volume of 0.930 cm<sup>3</sup>/g, and a BET surface area of 888 m<sup>2</sup>/g. From the BJH treatment of the adsorption data, the average pore diameter (4V/A) is 53.3 Å.

To generate the kernel needed for the PSD analysis, we have calculated a collection of individual adsorption isotherms,  $A_s$  (P,D), using the GCMC method, in a diameter range of  $0.75 \le D \le 20.0$  nm, with 55 different pore diameters. Calculations were performed at the experimental relative pressure data. Figure 2 shows six selected individual adsorption isotherms for pore diameters *D* = 1.5, 3.0, 4.5, 6.0, 7.5, and 14.0 nm. The narrowest pore shown, D = 1.5 nm, presents a 0-1 layering transition, whereas the wider pore, D = 14.0 nm, shows a monotonic intake with increasing pressure, as expected in nonporous materials. Intermediate pore sizes show the influence of the pore diameter over the capillary condensation step, the wider the pore the higher the capillary condensation pressure.





Figure 3. Discrete Picard condition, for different adsorption kernel sizes, as applied to the PHTS material. In all cases, the number of relative pressures is m = 29, and the number of pores are from left to right and from top to bottom n = 16 (a), 20 (b), 29 (c), 40 (d), and 30 (e). Circles correspond to the absolute values of the Fourier coefficients, crosses represent the singular values, and the lines correspond to a plot of the averages  $r_i$  for q = 1 (dotted lines) and q = 3 (continuous lines), all of them represented versus the number of pores in the selected kernels (n).

With the calculated set of individual adsorption isotherms, and based on the analysis of the DPC, our next step was to determine how many pores are needed to fit a given set of experimental data by means of a regularization procedure. Figure 3 shows how the DPC,  $r_i$ , and its components (i.e., the Fourier coefficients  $|\mathbf{u}_i^{\mathrm{T}}\mathbf{a}_e|$  and the singular values  $s_i$ ) vary for different adsorption kernels  $\mathbf{A}_{s}$  for the PHTS material. As a first approach to the problem, we decided to study four cases, keeping fixed the experimental number of relative pressures, m = 29, and selecting different sets of pore sizes, two with less pores than the number of pressure points, one with an equal number, and one with a greater number of pores (n = 16,20, 29, 40, first four cases in Figure 3). In all cases, the minimum and maximum pore diameter values were 0.75 and 14.0 nm, respectively; the selected pores included in the analysis were equally distributed between these two values. As it can be seen in Figure 3, besides the common oscillations beyond the gap in  $s_i$ , the fulfillment of DPC improves when increasing *n*. From the  $r_i$  averages, there is not a strong difference comparing q = 1 with q = 3. The kernel with n = 16 does not fulfill DPC, presenting a monotonic increasing trend (opposite to what it should be). As mentioned, this is the first criteria to be fulfilled. As previous results<sup>25</sup> showed, the small size of the kernels used seems to enhance fluctuations in the Fourier coef-



**Figure 4.** Global adsorption isotherms for different values of *n*. Diamonds correspond to the experimental values. The arrow denotes the change with increasing *n*. Inset a is the L-curve for n = 20, 29, and 40 (dashed line) and 30 (solid line), with symbols corresponding to  $\lambda_{\text{feas}}$ , +, \*,  $\Box$ , and  $\bullet$ , respectively. Inset b represents the average relative error (over 50 perturbations) of the obtained PSD *f* versus the index *n*. Symbols: for kernels  $29 \times 20, 29 \times 29, \text{ and } 29 \times 40; \bullet$ , kernel  $29 \times 30$ .

ficient. In general, we found for these sizes an initial increase in  $r_i$  for i = 0,1. Thus, the other three cases have a similar fulfillment of the DPC and the next criteria should be applied to all of them in order to discern the best one(s).

The second criterion would be the L-curve criteria. This is applied only to the kernels fulfilling the DPC condition. For the second, third, and fourth cases of Figure 3 (29 × 20, 29 × 29, and 29 × 40) we have observed that the values of  $\lambda_{\text{feas}}$  tend to increase monotonically as *n* increases (see the inset a) in Figure 4),  $\lambda_{\text{feas}} = 8.0, 8.7, \text{ and } 8.8$ . The residual error fluctuates as follows  $||\mathbf{a}_e - \mathbf{A}_e \mathbf{x}|| = 3.20$ , 1.94, and 1.96. The modulus of  $\mathbf{f}_{\lambda\text{feas}}$  decreases monotonically,  $||\mathbf{f}_{\lambda\text{feas}}|| = 0.675, 0.537, \text{ and } 0.458$ . Hence, according to the defined criteria, three of the a priori selected kernels (29 × 20, 29 × 29, and 29 × 40) fulfill DPC, whereas the 29 × 29 and 29 × 40 give similar L-curve and residual error. Hence, one would be able to chose between these two.

Although, in principle, we already have two feasible solutions, it is well-known that there are associated errors to the experimental data; it should be of relevance to know the effect these errors would have in the obtained PSD, showing the robustness of the procedure. As a third criterion, we have then calculated the effect of a Gaussian random error in the (experimental) data,  $\mathbf{a}_{e}^{*} = \mathbf{a}_{e} + \mathbf{e}$ . We have generated the error, e, after choosing its variance. This is done through a scaling factor *r* such that  $\mathbf{a}_{e}^{*} = \mathbf{a}_{e}(1)$ + rz), where z is a Gaussian random number. The value of r is chosen such that on average at least 99% of the perturbed values correspond to relative errors not greater than the experimental ones. The study is performed for the three kernels fulfilling the DPC. In these cases, we have chosen r = 0.02, and the average values over 50 realizations for the three kernels are  $||\mathbf{e}|| = 0.968, 0.90,$ and 0.968 with  $||\mathbf{e}||/|\mathbf{a}_{e}|| = 0.014, 0.013, and 0.014$ . Results for the case of PHTS and the kernels corresponding to Figures 3b,c, and d are summarized in Figure 4. The corresponding average values after perturbation are  $\lambda_{\rm feas}$  $= 8.16, 10.03, \text{ and } 10.30, ||\mathbf{a}_{e}^{*} - \mathbf{A}_{s}\mathbf{x}^{*}||_{2} = 3.38, 2.39, \text{ and}$ 2.45. The relative PSD variations on average are respectively  $||\mathbf{f}_{\lambda feas} - \mathbf{f}^*_{\lambda feas}||/||\mathbf{f}_{\lambda feas}|| = 0.102, 0.091, and 0.107$  (see inset b in Figure 4). As it can be observed, the shape of the corner seems to be better defined with increasing n.



**Figure 5.** Pore size distribution for four sizes of  $A_s$ , with and without a perturbation. Continuous lines correspond to results for unperturbed data, and dotted lines are a representative example of their corresponding perturbed cases. Each case can be distinguished from the height of the central peak over the continuous line, n = 20, 29, 30, and 40.

 Table 1. Summary of Relevant Results for the Studied

 Materials

material	pore range, nm	kernel size	$\lambda_{ ext{feas}}{}^a$	<b>Ax - a</b>    <sup>a,b</sup>	RPSDV <sup>b,c</sup>
PHTS SBA-15	$0.75 - 8.5 \\ 0.75 - 20.0$	$\begin{array}{c} 29\times 30\\ 38\times 41 \end{array}$	$\begin{array}{c} 10.0\\ 13.3 \end{array}$	$2.38 \\ 2.80$	0.09 0.28

 $^a$  Corresponds to an average over 50 realizations of the perturbation.  $^b$  Dimensions of  $||\mathbf{Ax} - \mathbf{a}||$  cm<sup>3</sup> STP/g.  $^c$  The relative PSD variation.

In fact, the 29 × 20 kernel exhibits a fuzzy corner. Inset b depicts the robustness of the calculated PSDs against perturbations in the experimental data. This robustness can also be observed in Figure 5, where the PSD is plotted for the above-mentioned values of *n* and their corresponding perturbation ||**e**||. The dotted lines in Figure 5 correspond to the case where a perturbation to ||**a**|| has been added, whereas the continuous lines correspond to the unperturbed cases. As can be seen in inset 4b, the 29 × 29 kernel is the most robust among the three studied here.

It is also observed in Figure 5 that the "noise" obtained in the PSD for wider pores decreases as n increases. In fact, the PSD vanishes at D = 8.5 nm, the noise appearing for higher values of D. Hence, although the previous 29  $\times$  29 kernel had the prescribed requirements, we have performed a further study with an additional kernel of 29 imes 30, taken from the 29 imes 40 one but including the pores just up to D = 8.5 nm. A study similar to the previous four kernels was performed (DPC, L-criteria, residual error values, and random errors into the experimental data). Results are also shown for completeness in Figures 3-5and in Table 1. This turned out to be the best among the five selected kernels in the present study. Results for the global adsorption isotherm as compared to the experimental data for PHTS with this selected kernel are shown in Figure 6, where we also show the corresponding PSD. The predicted adsorption behavior is found in excellent agreement with the experimental results. The calculated GCMC PSD presents a sound shape for these materials, with a narrow distribution of mesoporous around 57.5 Å, shifted in 17.0 Å to the right of the BJH average prediction. The left extreme of the PSD is attributed to the presence of the nano and micropores equal or smaller than 30 Å.<sup>19</sup>



Figure 6. (a) Nitrogen adsorption isotherm on PHTS at 77 K. Experimental (diamonds) and simulated (circles) results, with the best selected kernel. (b) The corresponding PSD: solid line with diamonds, BJH; dashed line with circles, GCMC + regularization using the selected adsorption kernel.

A similar analysis to the one explained by the PHTS material has been performed for the SBA-15 material. Figure 7 shows the influence of increasing the relative pressure values (from 0.925 up to 0.994) while keeping constant the number of pores in the selected kernels. The chosen pressure point values were 38 (up to  $p/p_0 = 0.925$ ), 40 (up to  $p/p_0 = 0.962$ ), 42 (up to  $p/p_0 = 0.981$ ), and 44 (up to  $p/p_0 = 0.994$ ), whereas the pore sizes were fixed to n =41, the minimum and maximum pore diameter values 0.75 and 20 nm. The selected pores included in the analysis were equally distributed between 0.75 and 9 nm, whereas in the range 9-20 nm, the pore diameters were separated by 1 nm. Figure 7a shows the experimental and simulated global adsorption isotherms for the four selected kernels  $(38 \times 41, 40 \times 41, 42 \times 41, \text{ and } 44 \times 41, \text{ respectively}),$ whereas the corresponding PSDs are shown in Figure 7b. A similar study to the one performed for the PHTS material (Figures 3-5) was performed for these four kernels (SVD, DPC, L-curve criteria, residual error values, and random error over the experimental data); graphical results are not shown here for brevity, numerical values are provided in Table 1. Among these four kernels, the one better fulfilling all criteria was the first one  $(38 \times 41)$ , which, in fact, is also the one in better agreement with the experimental adsorption isotherm (Figure 7a). Note, however, that the agreement for the rest of the kernels deteriorates only at high pressures, in which the abrupt raise of the curve is not captured by the simulated



**Figure 7.** (a) Nitrogen adsorption isotherm on SBA-15 at 77 K. The four figures represent the effect of increasing relative pressure values over the global adsorption behavior. Experimental (dashed lines) and simulated (solid lines) results. (b) The corresponding PSDs: solid line with circles, unperturbed case; dotted line, a selected perturbed case. In both figures, from left to right, from top to bottom, the kernel sizes are 38 × 41, 40 × 41, 42 × 41, and 44 × 41. The corresponding higher relative pressure for each kernel is shown in each figure. See text for details.

isotherm. We consider that this agreement could be improved, if needed, if additional pore sizes are included in the analysis, for which the whole procedure should be repeated. However, since the overall agreement is excellent and the obtained PSDs are sound, we decided to stop the procedure here. It is interesting to observe (see Figure 7b) that increasing the pressure does not affect the location



**Figure 8.** Snapshots of the adsorption process inside three individual pores D = 1.5, 6.0, and 14 nm, for selected relative pressures, (a)  $9.86 \times 10^{-3}$ , (b) 0.30, and (c) 0.95. Note that molecules in the wider pore are shown in reduced size with respect to the others.

of the mean peak of the PSD, representative of the mesopores forming the material, neither the nano- nor the microporous region. The effect is more noticeable in the right-hand side of the mean peak, in which the presence of wider pores is observed, contributing to an overall greater adsorption.

The calculated GCMC PSD for SBA-15 shows a sound shape in all cases, with a narrow distribution of mesopores around 70.0 Å, shifted in 16.7 Å to the right of the BJH average prediction (not shown here). As for the PHTS material, the left extreme of the PSD is attributed to the presence of the nano- and micropores, as already discussed.<sup>19,27</sup> Note, however, that the nano- and microporous

region was more relevant in the PHTS materials, probably due to the existence of plugged pores, which are contributing in the SBA-15 material, as unplugged, to the mesoporous region.

As a final comment, we should point out that excellent agreement for the global adsorption isotherm has been obtained for both materials following the simulationregularization procedure. The model used here for SBA-15 and that of Ravikovitch and Neimark<sup>27</sup> is the same; however, we did not observed the marked lavering transitions they obtained in the global adsorption isotherm obtained by NLDFT. Since in both cases smooth walls are used in the model, we can argue that the layering on their calculated adsorption isotherm may be a shortcoming of the approximations made in the theory they used. The simulation technique seems to be more accurate for these types of studies, despite the extra computing time. An additional advantage of using simulations is that the location of the molecules inside the pore is precisely known at any condition. This can help to elucidate the adequate conditions in which to run the experiments. For instance, the microporous range of the material could be better tracked if high-resolution adsorption isotherms are provided. This can be inferred just by observing the equilibrium configurations of selected pores at selected pressures, as shown in Figure 8. This figure shows snapshots of the adsorption process taking place inside individual pores of diameters D = 1.5, 6.0, and 14 nm, for selected relative pressures,  $9.86 \times 10^{-3}$ , 0.30, and 0.95 (Figure 8a-c, respectively). The lowest relative pressure corresponds to the first value at which the experiments were measured; note that the micropores are already filled at this pressure, whereas in the wider pores, a monolayer has already been formed. This would clearly affect the PSD and surface area calculations.

### **IV. Conclusions**

We have checked the validity of a combined GCMC simulation-regularization procedure for obtaining reliable PSD in two selected materials, SBA-15 and PHTS, synthesized in our laboratory. The a priori selection of these materials comes from their particular structure, with well-defined pore geometry and PSD with two distinct ranges (micro- and mesoporous), and also for their potential applications in several fields. The PSD analysis has been performed by a systematic methodology in which different mathematical and physical requirements should be fulfilled to select the feasible and more robust PSD.

In particular, PSDs were obtained by a deconvolution procedure in which a grid size evaluation and several choices of parameters were studied. Adding perturbations over the experimental adsorption data was used to check the robustness of the obtained PSD. The excellent agreement found between the calculated and the experimental adsorption isotherms corroborate the validity of the independent pore model for these materials and the method used to generate the kernel. The PSD provided by this procedure shows pore sizes in accordance to published values obtained from alternative experimental procedures, reassuring the validity of our methodology.

Finally, GCMC has proved to be a straightforward method, affordable nowadays, to generate the individual adsorption isotherms, more accurate and versatile done DFT approaches. It also provides additional insights into the best conditions to perform the experiments. A main advantage of using molecular simulations is that this methodology can be easily extended to investigate the behavior of other materials, and it can be an excellent tool to investigate the optimum conditions for specific applications of these materials, in a predictive manner.

**Acknowledgment.** We acknowledge the contribution to this work from our collaborators Sonia Abelló and Ilham Kirm. This research has been possible thanks to the

financial support received from the Spanish Government, under Projects PPQ2001-0671, REN2002-04464-C02-01, and CTQ2004-05985-C02-01. C.H. acknowledges a postgraduate Grant I3P from CSIC-MATGAS, Air Products.

LA050977N