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Adsorption of probe molecules in pillared interlayered clays: Experiment and computer simulation

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In this paper we investigate the adsorption of various probe molecules in order to characterize the porous structure of a series of pillared interlayered clays (PILC). To that aim, volumetric and microcalorimetric adsorption experiments were performed on various Zr PILC samples using nitrogen, toluene, and mesitylene as probe molecules. For one of the samples, neutron scattering experiments were also performed using toluene as adsorbate. Various structural models are proposed and tested by means of a comprehensive computer simulation study, using both geometric and percolation analysis in combination with Grand Canonical Monte Carlo simulations in order to model the volumetric and microcalorimetric isotherms. On the basis of this analysis, we propose a series of structural models that aim at accounting for the adsorption experimental behavior, and make possible a microscopic interpretation of the role played by the different interactions and steric effects in the adsorption processes in these rather complex disordered microporous systems. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4880962>]

I. INTRODUCTION

Pillared interlayered clays (PILC) have been the focus of intensive research for the last 20 years due to their potential applications as catalysts and their usage as molecular sieves.¹ This interest responds in particular to an attempt to design porous materials with larger pores than those of zeolites.

PILCs are synthesized by cation exchange in a cationic clay usually from the smectite group. The samples are later calcined by which pillars are created between the layers (also called lamellas²) of the original layered structure. In this way, the interlayer distance is fixed, with the practical advantage that the interlayer separation can be tuned by choosing the appropriate pillaring agent.

The system thus constructed is largely heterogeneous, by which its structural characterization poses a highly non-trivial problem. Whereas the interlayer distance is amenable to be determined by routine X-ray powder diffraction methods, the determination of the pillar distribution remains a somewhat elusive problem. Textural studies can be carried out by means of adsorption volumetry and microcalorimetry of selected probe molecules,³ which actually provide a quantitative picture of the pore volume and some hints as to how the pillars are distributed. Recently, the use of small angle neutron scattering combined with contrast matching techniques^{4,5} made possible the estimation of average interpillar distances, thus enabling an approximate quantitative approach to the problem of pillar distribution, but to date the number of studies on this problem remains scarce. This class of problems also presents

a considerable challenge to computer simulation and to theoretical approaches due to the presence of quenched disorder⁶ in the pillar distribution.

A number of theoretical and simulation works on the adsorption processes in pillared interlayered materials can be found in the literature. Molecular dynamics methods have been used to study the diffusion of adsorbates inside the pillared clays,^{7–10} whereas Monte Carlo simulation^{7,11–17} studies have essentially looked at the influence on the adsorption isotherms of the structural properties of the porous media, paying special attention to the pillar geometrical features: height, diameter, and shape. Regarding theoretical approaches, it is worth recalling in this context the work of Matusiewicz *et al.*¹⁸ based on Density Functional Theory (DFT) and those of Perez *et al.*¹⁹ and Pizio and Sokolowski²⁰ in which a combination of the inhomogeneous Ornstein-Zernike equation and the replica approach are employed to described disordered pillared clays. More recently Lomba and Weis²¹ have also considered by means of simulation and a replica Ornstein-Zernike approach a simpler situation in which the interlayer distance is short enough for the adsorbate-adsorbent system to be treated as a two dimensional system. Pizio *et al.*²² have studied the phase behavior of binary symmetric mixtures adsorbed in pillared slit-like pores using DFT. Finally, Olivier and Occelli²³ have employed a hybrid DFT method that considers a cylindrical model to estimate the pore size distribution from experimental isotherm data.

Here, we intend to carry out a study of two families of PILCs derived from Portuguese clay from Porto Santo and Ca²⁺-Na⁺ montmorillonite from Wyoming, designated hereafter by PTS and WYO, respectively. The pillarization process

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was carried out using ZrOCl_2 in solution, since the resulting PILCs have high hydrothermal stability, large interlayer spacing, and highly acidic sites.²⁴ A series of samples have been prepared with different concentrations of Zr cations, and volumetric and calorimetric adsorption experiments have been carried using N_2 , toluene, and mesitylene as probe molecules.

We have carried out extensive Grand Canonical Monte Carlo (GCMC) simulations of N_2 , toluene, and mesitylene in a series of relatively simple models of PILCS constructed on the basis of the information obtained from the adsorption experiments. A detailed analysis of the experimental adsorption results in the light of the computer simulation study, will furnish a microscopic picture of the PILC structure and the adsorption process. Besides, one PTS sample has been selected to perform neutron diffraction experiments in the intermediate to high scattering wavenumber region. The extension of the explored spatial scales towards the microscopic range, as compared to those typical of a standard small angle setup, opens the possibility of a precise structural analysis by means of the concomitant use of computer modeling. However, within the computational model used here, the neutron measurements although compatible with the adsorption results do not yield a clear structural discrimination. At any rate, they represent a clarifying initial approach for a more sophisticated modeling.

The rest of the paper is organized as follows. Section II is devoted to a description of the sample preparation and adsorption experiments. The PILC model and the analysis of its topological properties are to be found in Sec. III. Details of the computer simulation procedure are described in Sec. IV. In Sec. V the results of adsorption simulations for the proposed models are presented and compared with the experimental data. Finally, in Sec. VI we discuss our neutron scattering experiment results in the light of the computer simulation and volumetric/microcalorimetric adsorption data. Our most significant conclusions and future prospects are presented in Sec. VII.

II. SAMPLE PREPARATION AND ADSORPTION EXPERIMENTS

The parent materials for the PILC synthesis were obtained from samples of soils from deposits of Porto Santo-Madeira archipelago-(PTS) which contain 93% of clay mineral, together with commercial samples of montmorillonite from Wyoming (WYO) (Volclay SPV-200 from American Colloid Company). The samples were treated with a fresh solution of oligomer of ZrOCl_2 (Merck, 99% pure) at varying concentration (see Table I). Following the procedure indicated in Refs. 3 and 24, we finally obtained a series of samples in which the interlayer separation, (i.e., the pillar height, h_p) was determined by X-ray diffraction. The chemical composition of the samples, in particular the amount of Zr incorporated into the PILC structure was determined using atomic absorption spectroscopy. In Table I it can be appreciated that despite the substantial differences in Zr concentration in the initial solution during the pillarization process, the amount that gets into the PILC is very similar in all samples. The most significant variations are found for the WYO-2

TABLE I. Properties and designation of the PILC samples under study. In the sample names the acronyms PTS and WYO indicate the parent clay, $[\text{Zr}]_s$ designates the Zr concentration in solution during the ionic exchange reaction, and $[\text{Zr}]_p$ is the final concentration in the dried PILC samples. BET specific surface area and micropore volumes were calculated from N_2 volumetric adsorption experiments at 77 K.

Sample	$[\text{Zr}]_s$ (mmol/g)	$[\text{Zr}]_p$ (mmol/g)	A_{BET} (m^2/g)	V_{micro} (cm^3/g)
PTS-1	1.8	1.71	269	0.097
PTS-2	2.5	1.73	298	0.106
PTS-3	4.0	1.73	335	0.121
WYO-1	1.8	1.71	266	0.101
WYO-2	2.5	1.87	266	0.103
WYO-3	4.0	2.01	204	0.077

and WYO-3 samples. From the Zr concentration in the dried PILC samples (Table I), and using the theoretical surface area of a smectite,²⁵ the pillar density (in pillars/ nm^2) was calculated considering the zirconium tetrameric cations as the intercalating species.²⁶ Notice, however, that there is not a clear consensus^{14,27,28} regarding this point.

Adsorption volumetric and microcalorimetric experiments were performed using a conventional volumetric apparatus coupled to a Tian-Calvet microcalorimeter (model C80, Setaram, France). N_2 adsorption experiments were carried out at 77 K and toluene and mesitylene measurements at 315 K. In the case of N_2 adsorption only volumetric experiments have been carried out, since the experimental setup was not prepared to perform calorimetric measurements at 77 K. From N_2 adsorption isotherms we have determined the micropore volume, and the apparent BET specific surface area, which are collected in Table I. Using this geometric information, we have evaluated the corresponding packing densities of toluene and mesitylene. These quantities are presented in Table II together with the relative packing densities referred to the density of the bulk liquid at the same temperature at which the adsorption experiment was performed. Other relevant information on the PILC samples; namely pillar heights, h_p , and pillar densities, ρ_p ; are also included in Table II.

From all these results, we can appreciate that the WYO samples have an interlayer separation significantly larger than the PTS samples, which will be shown to have an important effect regarding the packing of aromatic molecules. BET areas are similar being the largest one (and largest micropore volume) that of PTS-3 sample. The lowest values correspond to the WYO-3 sample, which also has the largest pillar density. Interestingly, one can observe that despite the relatively small differences in pillar density ($\approx 20\%$) changes in micropore volume rise up to $\approx 50\%$. This implies that a substantial change in the topology of the micropore network must be taking place. An interesting feature that is readily seen in Table II is that, when packing aromatic molecules, the WYO samples are considerably more efficient than the PTS ones, probably due to their larger interlayer separation. In particular, it is striking that the sample WYO-3, which has the smallest micropore volume is the one that packs the largest amount of toluene (and for which mesitylene also reaches the largest packing fraction in the micropores). In the case of toluene, the

TABLE II. Topological information on the PILCS samples: Pillar height, h_p , and density of pillars ρ_p ; and results of toluene and mesitylene microcalorimetric adsorption experiments. $n_{\mu p}$ is the amount of adsorbate that fills up the micropores, d_{pck} is the molar packing density, and d_{pck}/d_{liq} is the ratio of the packing density inside the micropores with respect to that of the bulk liquid.

Sample	h_p (nm)	ρ_p (nm ⁻²)	$n_{\mu p}$ (mmol g ⁻¹)		d_{pck} (mmol/cm ³)		d_{pck}/d_{liq}	
			Toluene	Mesitylene	Toluene	Mesitylene	Toluene (%)	Mesitylene (%)
PTS-1	0.71	0.60	0.605	0.290	6.24	2.99	69	38
PTS-2	0.70	0.61	0.470	0.250	4.43	2.36	48	30
PTS-3	0.70	0.61	0.610	0.330	5.04	2.72	55	34
WYO-1	0.85	0.60	0.680	0.440	6.73	4.36	73	55
WYO-2	0.85	0.67	0.725	0.410	7.04	3.96	77	50
WYO-3	0.78	0.73	0.740	0.390	9.61	5.06	105	64

packing is so efficient that the bulk liquid density is recovered. In what follows we will see to what extent these features can be captured and explained by our computer models.

III. COMPUTER MODELING

In the present study we have used the model introduced in a previous work.²⁹ The PILCS are represented as slit pores with cylindrical pillars placed between flat walls. The walls represent the surface of the clay layers. The cylinder axes are perpendicular to the wall surfaces (see Figure 1); and pillar configuration without positional order are considered. In order to analyze the topological properties of the model we will first focus on a further simplified version in which only repulsive interactions (which are the source of all steric constraints for the adsorbate molecules) will be taken into account. The purpose of this approach is to consider the ability of different adsorbates to diffuse inside the porous media as a function of the pillar diameter, σ_p , and to estimate upper bounds for this parameter.

The adsorbate molecules, considered here as spherical particles, inside our idealized PILC will be confined by an external potential with the following contributions:

$$V_{ext}(\mathbf{r}_i) = V_w(z_i) + V_p(\mathbf{r}_i; \{\mathbf{R}_p\}), \quad (1)$$

where V_w contains the adsorbate-wall interactions and V_p includes the interactions between one adsorbate molecule and

the pillars of the system. $\{\mathbf{R}_p\}$ stands for the spatial configuration of the pillars described in terms of their (X_k, Y_k) coordinates, and $\mathbf{r}_i$ denotes the adsorbate position. With the z -axis defined to be perpendicular to the clay layers, z_i determines the distance between the adsorbate and the layer at the origin. For the adsorbate-pillar interaction we consider

$$V_p(\mathbf{r}_i; \{\mathbf{R}_p\}) = \sum_{k=1}^{N_p} \Phi_p(\mathbf{r}_i, \mathbf{R}_k), \quad (2)$$

with

$$\Phi_p(\mathbf{r}_i; \mathbf{R}_k) = \begin{cases} 0 & r_{ik} \geq (\sigma_p/2 + \sigma_a/2) \\ \infty & r_{ik} < (\sigma_p/2 + \sigma_a/2). \end{cases} \quad (3)$$

In (2) and (3) N_p is the number of pillars, $\mathbf{R}_k$ describes the position of the k th pillar, and $r_{ik} = [(x_i - X_k)^2 + (y_i - Y_k)^2]^{1/2}$. σ_p is the diameter of the pillar, and σ_a is the diameter of the probe molecule, which is related with the molecule's largest interaction site in the models that will be used to study the adsorption processes. Additionally, the adsorbate-wall potential will also be given by a hard core interaction

$$V_{fw}(z_i) \equiv V_{fw}^{rep}(z_i) = \begin{cases} 0 & \sigma_a/2 \leq z_i \leq h_p - \sigma_a/2 \\ \infty & \text{otherwise} \end{cases}, \quad (4)$$

where h_p is the interlayer separation. Finally, adsorbate molecules can interact through a Lennard-Jones (LJ) pair potential, $\phi_{LJ}(r)$,

$$\phi_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (5)$$

with r being the distance between molecules, and σ and ϵ are the well-known length (diameter) and energy parameters of the LJ potential.

For many purposes, a PILC can be considered as a quasi-two-dimensional system because adsorbate molecules are constrained to move between two walls whose separation is typically within the range of a few adsorbate molecular diameters. Additionally, the disordered distribution of pillars can be taken as a case of quenched disorder, where the pillars are “frozen” while the adsorbate species are allowed to move inside the micropore cavities and reach thermodynamic equilibrium. The PILC model and the adsorbate molecules as a whole are to be deemed as a partly quenched system.⁶ Following Ref. 29 pillar configurations in the two dimensional

FIG. 1. Sketch of the micropore model: two parallel walls represent the clay layers and cylindrical pillars play the role of the intercalated cationic columns.

FIG. 2. Schematic representation of the AUA models for toluene (a) and mesitylene (b). Figures on the left illustrate the shift of the interaction sites for CH and CH₃ with respect to the geometrical centers. Figures on the right illustrate united atom groups by means of spheres of different colors: yellow (CH₃), light blue, (CH), and dark blue (tertiary C).

space of the layer plane are generated from Monte Carlo simulations in the canonical ensemble of hard core models.

When modeling microporous materials we must consider two important concepts: available and accessible volumes. In our particular model, a two-dimensional distribution of disks (the projection of the pillars onto the layer plane) and the interlayer separation completely determine the micropore volume. Bearing this in mind, available volume refers to those portions of the microporous sample in which a given probe molecule can be placed without steric hindrance from pillars or walls. In contrast, accessible volume refers to those positions inside the available volume that the probe molecule can reach and diffuse to throughout the system. Accessible volumes can be evaluated by means of a topological analysis²⁹ of the porous sample in which the system volume is divided into portions using a Delaunay tessellation³⁰ referred to the pillar centers. These portions (regular triangular prisms) can be thought as triangles by attending to their projection on the surface walls. The pillar centers define the vertices of those triangles. A percolation analysis is carried out on the clusters of connected neighboring Delaunay triangles (by connected we mean that a molecule can diffuse directly from one triangle to the other without being blocked by pillars). The sample is said to be accessible to the probe molecule when, at least, one cluster connecting neighbor triangles percolates.^{29,30}

In order to perform this type of analysis we need to define an accessibility interpillar distance, $d_p = \sigma_p + \sigma_a$ for each probe molecule. This quantity represents the maximum separation between two pillars that would block the passage of a probe molecule between them in any possible orientation. For the case of N₂ we have used $\sigma_a(\text{N}_2) = \lambda \sigma_{NN} = 0.3$ nm, where σ_{NN} is taken from the value of the distance parameter of a N₂ two-center LJ model.³¹ and we considered $\lambda = 0.9$. This latter choice will be justified below. Toluene molecules were represented by a non-polar anisotropic united atom (AUA) model³² in which the CH₃, and CH groups, and the tertiary C of the molecule are represented by a single interaction site each, as shown in Figure 2(a). In this case, when considering the molecule in the most favorable orientation to diffuse between two adjacent pillars, it is precisely the size of the methyl group which determines the accessibility diameter, by which we have defined $\sigma_a(\text{Tol}) = \lambda \sigma_{\text{CH}_3-\text{CH}_3} = 0.325$ nm.

Considering the geometry of the mesitylene molecule (see Figure 2(b)), the same accessibility diameter holds, and consequently the analysis that follows applies to this probe molecule as well.

The factor λ accounts for softness of the LJ cores, and formally it can be explained in terms of the physics of colloids by means of a Hamaker-like analysis³³ in which each pillar is modeled as a continuum of particles, with an effective density ρ_c confined inside a cylinder of radius r_{cyl} . That continuum interacts through Lennard-Jones potential, $\phi_{LJ}(r|\sigma, \epsilon)$: with parameters ϵ_c, σ_c , with other pillars and with parameters $\epsilon_{ic}, \sigma_{ic}$ with the adsorbate sites of type i . Under this framework, using some approximations regarding the pillar length, and considering for simplicity $\sigma = \sigma_{ic} = \sigma_c$ one finds by numerical integration a pillar-pillar interaction, $\Phi_{\text{cyl-cyl}}(r)$ very repulsive at short distances, and with a short range attractive tail. From this interaction one can extract a hard-sphere effective diameter for the pillars $\sigma_p \simeq 2r_{\text{cyl}} + \sigma/2$. The effective interaction between cylinders and adsorbate molecules, $\Phi_{\text{cyl-mol}}(r)$ can be written as a function of the distance x between the adsorbate and the surface of the cylinder, $x = r_{ic} - r_{\text{cyl}}$. This interaction has a minimum at $x_{\text{min}} \simeq 0.86\sigma$, and it is equal to zero at $x_0 \simeq 0.72\sigma$ (these numbers can vary slightly with r_{cyl}/σ). Attending to these results we obtain that the adsorbate-pillar interaction is repulsive for distances below $\sigma_{ip} \simeq \sigma_p/2 + 0.47\sigma \approx (\sigma_p + \sigma)/2$. The value of λ should then be defined by looking for the interpillar distance at which the crossing rate of adsorbate molecules between two pillars vanishes which, in addition to the possible energy barrier defined by the particle-pillar interactions at short interpillar distances, will depend on temperature. After some tests using Molecular Dynamics simulations on related two dimensional systems we found that a value of $\lambda \simeq 0.90$ can be considered appropriate for a reduced temperature $k_B T/\epsilon \approx 1$ (with k_B being the Boltzmann constant).

A. Percolation analysis

With the definitions of the accessibility probe diameters, σ_a in mind, we can now focus on another quantity of interest, namely, the threshold pillar diameter σ_{per} . For a given pillar distribution and adsorbate, we define $\sigma_{\text{per}}(\sigma_a)$ as the

minimum pillar diameter for which the porous media becomes inaccessible for the adsorbate, i.e. there is not any percolating cluster of available Delaunay triangles. This implies that the molecules will not be able either to enter into the microporous region or to diffuse through the sample; $\sigma_{per}(\sigma_a)$ provides a direct information regarding the potential applications of the sample to act as a molecular sieve for a given adsorbate.

In practice, $\sigma_{per}(\sigma_a)$ is computed by means of a finite size-scaling analysis on the fraction of accessible configurations. This quantity will be evaluated for a collection of pillar configurations with the same pillar density corresponding to different realizations of quenched disordered pillars for a series of pillar diameters and sample sizes ranging from $L = 10$ nm (a total of 4000 configurations) to $L = 70$ nm (500 configurations). We have considered three types of pillar configurations.²⁹ These have been generated using equilibrium simulations of plain hard disks or hard disks interacting with an additional Yukawa potential, either attractive or repulsive. Our analysis of the simulation results (see Sec. IV) led us to conclude that the available experimental data do not allow to discern between these alternatives, and therefore we will present the results for the pillar distributions obtained from quenched configurations of plain hard disk simulations. We can take advantage of the “self-averaging” property⁶ of these systems. This implies that, as the sample size becomes larger, more realizations of the disorder are implicitly accounted for in a given quenched configuration. Therefore, for larger samples a smaller number of pillar configurations can be used without affecting the statistical quality of the result.

The finite-size scaling analysis was carried out by locating for each system size, the pillar diameter $\sigma_{per}(L)$, for which the fraction of accessible configurations is one half. These results are used to extrapolate the threshold pillar diameter in the thermodynamic limit $\sigma_{per} = \lim_{L \rightarrow \infty} \sigma_{per}(L)$, through the scaling equation^{30,34}

$$\sigma_{per}(L) = \sigma_{per} + aL^{-1/\nu}, \quad (6)$$

where a is an adjustable parameter and ν is the correlation length exponent of percolation transitions, that for two-dimensional system is known³⁰ to be $\nu = 4/3$. The results are shown in Table III. As expected the distributions with higher pillar densities lead to smaller threshold pillar diameters. Taking into account these results, in our modeling of adsorption processes using GCMC simulations we will consider values of the pillar diameter below the threshold value, σ_{per} , for the corresponding adsorbate.

TABLE III. Threshold pillar diameter $\sigma_{per}(\infty)$ calculated for two adsorbates with different accessibility probe diameters, σ_a , and various pillar densities corresponding to those estimated for the PILC samples. PTS refers to the three PILC samples derived from PTS clay.

Sample(s)	$\rho_p(\text{nm}^{-2})$	$\sigma_{per}[\text{N}_2](\text{nm})$	$\sigma_{per}[\text{tol}](\text{nm})$
PTS; WYO-1	0.60	0.9656(10)	0.941(4)
WYO-2	0.67	0.901 (4)	0.875(4)
WYO-3	0.73	0.8515(24)	0.827(3)

FIG. 3. Fraction of available area, ϕ_{av} (filled symbols, upper curves) and accessible area, ϕ_{ac} (empty symbols, lower curves) for different system sizes (see the corresponding symbols in the Legends) as a function of the pillar diameter for a pillar distribution generated from hard disks configurations with a density $\rho_p = 0.60 \text{ nm}^{-2}$ (samples PTS and WYO-1). Lines connecting the symbols are drawn as a guide to the eye. The accessible area exhibits a percolation transition and it is expected to vanish in the thermodynamic limit at $\sigma_p \simeq 0.966 \text{ nm}$, whereas the available area results hardly depend on the system size and remain finite in the whole range of σ_p values.

Let us now focus on the calculation of the available and accessible volume of systems with different pillar configurations. It is worth mentioning that the use of areas or volumes is almost equivalent, since accessible volume can be obtained from the accessible area result just by multiplying by a factor that depends on the interlayer distance, h_p , and the molecular diameter σ . The calculations are carried out using a standard Monte Carlo one-particle insertion method.⁶ The fraction of available area is computed evaluating the fraction of successful particle insertions (those with $V_p(\mathbf{r}_i) = 0$ in Eq. (2)). In order to compute the fraction of accessible area only the successful insertions that happen in positions belonging to triangles previously marked as accessible in the percolation/connectivity analysis of the microporous sample will be taken into account.

As a test-case we have considered the models of N_2 cited above. In the insertion attempts we considered a molecular diameter $\sigma_{test} = 0.37 \text{ nm}$, which is nothing but the σ parameter of a one-site LJ model for nitrogen,¹⁰ whereas the connectivity of the pore network (percolation analysis) was carried out using $\sigma_a = 0.30 \text{ nm}$. In Fig. 3 we plot the fractions of available, $\phi_{av}(\sigma_p)$, and accessible, $\phi_{acc}(\sigma_p)$ areas. Consistently, we find $\phi_{av}(\sigma_p) > \phi_{acc}(\sigma_p)$; reflecting the presence of a non-negligible portion of inaccessible voids in the porous structure. One immediately appreciates that the fraction of accessible area curves initially depend linearly on the pillar diameter (0.85–0.90 nm), up to a point where they drop rapidly to zero, exhibiting a significant size dependence. Actually, this behavior closely resembles that of the fraction of accessible configurations,²⁹ with an intersection point which defines the threshold pillar diameter in both cases. In contrast, the fraction of available area has an almost linear dependence on the pillar diameter. Both quantities $\phi_{av}(\sigma_p)$ and $\phi_{acc}(\sigma_p)$ depend on the test particle used.

IV. ADSORPTION SIMULATIONS

As mentioned before, we have carried out GCMC simulations on models of PILCS in order to provide microscopic insight into the processes of adsorption of several probe molecules, and thus provide a microscopic interpretation for the experimental results of Sec. II.

Our approach has two obvious limitations. First, PILCs are formed by microcrystallites of hundreds of nanometers in size, that are well beyond the maximum size accessible to our computing capabilities (tens of nm). This implies that we will not be able to account for the effects of correlations in the porous system beyond a few nm. Additionally, we lack a clear physicochemical picture of the pillarization process, and hence the pillar distribution is mostly unknown. At present, neutron scattering contrast matching techniques can provide at maximum an estimate of the average interpillar distance. Given this situation, and the fact that at our approximation level we could not discern between the various types of pillar distributions we have explored, we decided to employ the pillar diameter as the quantity to be tuned in order to fit the porosity of our model systems to that of the adsorption volumetry experiments. Experimental knowledge concerning the size, shape (and even detailed composition) of the pillars^{27,28} is very limited (even the pillar height exhibits a certain variability). In fact one can assume that within certain physicochemical limits this quantity can be considered as an adjustable parameter of the model. This is the approach we have adopted here.

A. The potential model

The total potential energy U_T of the adsorbate molecules confined inside the micropores of the PILCs is given by

$$U_T = U_p + U_w + U_A, \quad (7)$$

namely, the adsorbate-pillar interaction U_p , the adsorbate-wall potential energy U_w , and the adsorbate-adsorbate intermolecular potential energy U_A . This last term can be expressed as

$$U_A = \sum_{a < b} \sum_{i \in a} \sum_{j \in b} \phi(r_{ij}; \epsilon_{ij}, \sigma_{ij}), \quad (8)$$

where N_A is the number of adsorbate molecules and N_c is the number of interacting centers per molecule. Subscripts a and b refer to adsorbate molecules, whereas i and j represent interaction sites, and r_{ij} is the distance between sites. The pair potential ϕ_{LJ} is a cut and shifted LJ potential

$$\phi(r) = \begin{cases} \phi(r) - \phi(r_c); & r < r_c \\ 0; & r \geq r_c \end{cases}; \quad (9)$$

and r_c is the cut-off radius. Cross-interactions are defined as usual in terms of the Lorentz-Berthelot (LB) mixing rules.^{35–37}

As mentioned before, we have chosen the non-polar AUA model³² to describe the intermolecular interactions, both in toluene and in mesitylene. At first glance disregarding the charges may seem too simplistic, however, a number of

works^{32,38} have shown that the electrostatic contributions in aromatic molecules represent approximately less than 10% of the total intermolecular energy. This explains why such a model is able to describe correctly liquid-vapor equilibrium. Regarding the adsorbate-adsorbent interactions, taking into account the simplicity of our model, the consideration of more complex interactions such as electrostatic potentials would not yield significantly different results from those obtained here with the adsorbate-adsorbent potentials that we will define below, being steric effects most likely dominant in the adsorption behavior. We expect anyway, that the leading effects of the charge-quadrupole and charge-octupole interactions are effectively incorporated by the fitting of potentials to experimental data.

The total adsorbate-wall potential energy is given by

$$U_w = \sum_{i=1}^{N_s} [\Phi_w(z_{ai}) + \Phi_w(H_p - z_{ai})], \quad (10)$$

where $N_s = N_d N_c$ is the total number of interaction sites; z_i is the distance between the interaction site i and one of the model walls, and the potential Φ_w is described by the 10–4–3 potential of Steele,³⁹

$$\Phi_w(z_i) = A \left[\frac{2}{5} \left(\frac{\sigma_{iw}}{z_i} \right)^{10} - \left(\frac{\sigma_{iw}}{z_i} \right)^4 - \frac{\sigma_{iw}^4}{3\delta(z_i + 0.61\delta)^3} \right], \quad (11)$$

with $A = 2\pi\rho_w\epsilon_{iw}\sigma_{iw}^2\delta$, where δ is the separation between lattice planes within a layer, and ρ_w , the layer density. The parameters σ_{iw} and ϵ_{iw} are cross-interaction parameters that are calculated using the LB rules, e.g., $\epsilon_{N_2-w} = \sqrt{\epsilon_w\epsilon_{N_2}}$ and $\sigma_{N_2-w} = (\sigma_w + \sigma_{N_2})/2$. For σ_w we use $\sigma_w = 0.262$ nm, which corresponds to the LJ diameter of oxygen anions on the silicate layer. The atomic density of the clay sheet is $\rho_w = 303.8$ nm^{−3} and the distance between lattice planes within a PILC layer⁴⁰ is $\delta = 0.216$ nm. The value of ϵ_w has been used as an adjustable parameter.

The remaining adsorbate-adsorbent contribution is due to the pillars, and it is expressed by Eq. (2), where Φ_p is taken now as

$$\Phi_p(r_{ik}) = \begin{cases} \infty; & r_{ik} < \sigma_{ip} \\ \varphi_{ip}(r_{ik}) - \varphi(\sigma_{ip} + x_c); & \sigma_{ip} \leq r_{ik} \leq \sigma_{ip} + x_c \\ 0; & r_{ik} > \sigma_{ip} + x_c, \end{cases} \quad (12)$$

where

$$\varphi_{ip}(r) = -\epsilon_{ip} \exp[-\kappa_p(r - \sigma_{ip})]. \quad (13)$$

As before, ϵ_{ip} and σ_{ip} are cross-interaction parameters calculated using the LB rules, and κ_p is a screening parameter which determines the range of the interaction, and x_c is a cut-off distance parameter. The interaction of the aromatic rings of toluene and mesitylene with the acidic sites in the pillars is mostly due to the π -electrons, by which is clearly of quantum mechanical nature, and most likely short ranged and intense at short distances. Therefore, in our calculations we have resorted to this simple exponential interaction (12), similar to the wall-adsorbate interaction of Ref. 41. Attempts to fit the adsorption results to pillar-adsorbate potentials modeled with

TABLE IV. Parameters of the interaction potentials employed for nitrogen, toluene and mesitylene molecules. The geometric disposition of the interaction sites for toluene and mesitylene can be viewed in Fig. 2, r_c is the cut-off distance for the Lennard-Jones interactions.

Model	Site	σ (nm)	ϵ/k_B (K)	r_c
one-site LJ potential (nitrogen) ¹⁰	N ₂	0.37	95.05	$3\sigma_{N_2}$
AUA non-polar (toluene ³² and mesitylene)	CH	0.32464	89.415	$4\sigma_{CH}$
	C	0.30648	42.079	$4\sigma_{CH}$
	CH ₃	0.36072	120.15	$4\sigma_{CH}$

LJ chains, or integrated expressions like the Steele potential or more complex alternatives⁴² were unsuccessful.

B. Simulation details

Our main goal in the simulation work is to find a set of adjustable parameters of the model (σ_p , ϵ_w , κ_p , ϵ_p) that provide a good or, at least, a semi-quantitative description of the experimental results. In order to attain such a goal we have resorted to a trial and error strategy. The parameters for the adsorbate-adsorbate interaction are taken from the literature and collected in Table IV.

The adsorption process was modeled using GCMC simulations, at the desired temperatures, T , chemical potential, μ , and sample volume, V . The simulation box has a cuboid shape whose volume is given by $V = h_p A$, where h_p is the separation between the walls (i.e., the pillar height) and A is the area parallel to the walls, which corresponds to a square surface ($A = L^2$). The pillar main axis defines the z -axis and the system has periodic boundary conditions in the x , y directions. The box dimension is defined by L , which is set to 10 nm in all our calculations. For the pillar height we have used the corresponding experimental values for each sample. At this point, it is worth mentioning that our model aims at accounting only for the microporous adsorption. Our sample is infinite along the x and y directions and cannot account for adsorption at external surfaces or into the mesopores formed in the experimental sample by the aggregation of PILC microcrystallites. On the other hand, from the experimental point of view, the region of micropore adsorption is well characterized in these and related systems by the behavior of the isosteric heats of adsorption.³ Comparisons simulation/experiment must be performed within this region.

According to the GCMC methodology, the chemical potential of the adsorbate within the sample micropores is the same as that of the bulk adsorbate in an external reservoir in equilibrium with the adsorbed sample. The pressure, p , of the gas in that reservoir can be identified with the experimental pressure measured in the adsorption experiment. We are working at sufficiently low pressures so that the ideal gas law can be used to calculate the pressure from the chemical potential of our GCMC simulation. Otherwise, it should be possible to resort to a Redlich-Kwong⁴³ or to a Benedict-Webb-Rubin^{44,45} equation of state if corrections were needed. The results for the isotherms will be given as a function of the ratio p/p_0 , where p_0 is the saturation pressure of the adsorbate at the corresponding temperature.

N₂ adsorption simulations are carried out at 77 K ($p_0(\text{N}_2) = 95.15$ kPa).⁴⁶ Toluene and mesitylene adsorption measurements and simulations are performed at 315 K and their respective saturation pressures are^{47,48} $p_0(\text{tol}) = 8.56$ kPa and $p_0(\text{mes}) = 0.935$ kPa. All calculations are carried out at a series of chemical potentials until the adsorption reaches a plateau, where the micropore volume can be considered to be filled.³ One must bear in mind that in the case of the experiments, after micropore filling adsorption continues on external surfaces of the microcrystallites and mesopores, a feature that we cannot aim at reproducing.

In order to get a consistent representation of the disordered structure of the pillars, we have to average over quenched disorder, and therefore for each given case (μ , V , T) we have performed simulations over 10 pillar configurations, randomly chosen from a series of frozen hard disk configurations consistent with the experimental pillar density. In the GCMC simulations the adsorbate molecules are only allowed to occupy the accessible volume regions, which are located, as explained above, using a Delaunay tessellation. Additionally, the pillar configurations used in the simulations are chosen from those characterized as accessible (as explained in Sec. III A). This bias is removed correcting the final thermodynamic averages taking into account the fraction of accessible configurations previously calculated for a given type of pillar distribution—characterized by ρ_p and σ_p . For each of the 10 pillar configurations, we run 4×10^6 GCMC cycles (particle insertion/deletion attempts, and subsequent translations/rotations of all adsorbed particles), and thermodynamic averages are calculated along the last half of the run. Isosteric heats of adsorption are calculated following the prescription of Ref. 49.

Finally, some of the quantities obtained from experiments, such as the amounts adsorbed, $n_{\mu p}$, or the micropore volume, $V_{\mu p}$ are expressed relative to the PILC mass. In our model, we approximate the mass of our system using the density of the Wyoming clay,⁵⁰ $\rho_{PILC} = 2.457$ g/cm³, as average density for all PILC constituents (both layers and pillars).

V. RESULTS

In this section, we bring the computational approach in contact with the experimental results and construct our model. The first step in this direction is the study of the nitrogen adsorption, the basic probe molecule to analyze the porous geometry of our samples.

A. Nitrogen adsorption simulations

As mentioned, nitrogen adsorption volumetry is an extended technique used to measure the volume of the micropore cavities. N₂ is inert, its molecules are small and for many purposes can be considered almost spherical (the ratio of the bond length and the LJ diameter is approximately 0.33) and therefore one can assume N₂ molecules can probe most micropore cavities in the sample. As a first step we should determine the wall-adsorbate and pillar-adsorbate parameters of our model. Unfortunately, we cannot resort to the fitting of

TABLE V. Geometric characteristics of the PILC samples. Diameters are estimated from the fittings of the calculated and experimental volumetric adsorption isotherms to the pillar model considered in this work.

	PTS-1	PTS-2	PTS-3	WYO-1	WYO-2	WYO-3
$\sigma_p(\text{N}_2)(\text{nm})$	0.92	0.91	0.87	0.91	0.85	0.84
$\sigma_p(\text{toluene})(\text{nm})$	0.93	0.94	0.92	0.92	0.86	0.81
$\sigma_p(\text{mesitylene})(\text{nm})$	0.94	0.94	0.93	0.94	0.87	0.82

isosteric heats of adsorption, since our present facilities do not allow for measurements at 77 K. We have thus concentrated on the volumetric isotherm at low pressures to get a rough estimate for the particle-wall interaction: $\epsilon_w/k_B \simeq 30$ K, and we have tuned the value of σ_p to give account of the experimental results for the micropore volume (see Table V). Results are presented in Table VI.

B. Toluene adsorption simulations

In the case of toluene, the adjustable parameters of the model are estimated by taking into account the low coverage behavior of the volumetric and microcalorimetric isotherms, i.e., both amounts adsorbed and isosteric heats of adsorption, q_{st}^σ . We get $\epsilon_w/k_B \simeq 5$ K, $\epsilon_p/\epsilon_{CH} = 40$, and $\kappa_p = 10.77 \text{ nm}^{-1}$. Pillar diameters, σ_p , are adjusted to reproduce the experimental packing densities, which are calculated using the amounts adsorbed at micropore filling completion and the pore volume estimated in the N_2 adsorption volumetry (see Table V). Paying attention to the calorimetric curves for toluene it became clear that it was necessary to consider a short range attraction between the pillars and the adsorbate. An example of the results is presented in Figure 4 for sample WYO-3.

Note that the values of ϵ_p are several orders of magnitude larger than ϵ_w . This is due to the fact that ϵ_w enters into the interaction through the prefactor A in Eq. (11). When inserting the values of ϵ_w , and ϵ_p in (11) and (12) one finds that pillar-wall and pillar-layer interactions are now of the same order of magnitude. Their respective net contributions to the isosteric heats will be seen to reach similar values for medium

TABLE VI. Results of adsorption simulations for N_2 , toluene, and mesitylene. The micropore volume, $V_{\mu p}^{sim}$, is estimated using only the N_2 adsorption simulation (in parallel with the experimental procedure), ($n_{\mu p}^{sim}$) is the total amount adsorbed on the micropores in the simulation. This table is to be compared with the experimental results of Tables I and II.

Sample	$V_{\mu p}^{sim} (\text{cm}^3/\text{g})$ N_2	$q_{pck}^{sim} (\text{mmol}/\text{cm}^3)$		$n_{\mu p}^{sim} (\text{mmol}/\text{g})$	
		Toluene	Mesitylene	Toluene	Mesitylene
PTS-1	0.096(6)	6.0(11)	3.4(7)	0.58(8)	0.33(7)
PTS-2	0.106(5)	4.6(11)	3.1(8)	0.49(9)	0.33(7)
PTS-3	0.122(4)	5.6(18)	3.0(8)	0.68(7)	0.36(8)
WYO-1	0.107(5)	6.8(10)	4.1(7)	0.73(7)	0.44(6)
WYO-2	0.104(5)	6.4(12)	4.5(9)	0.67(9)	0.47(7)
WYO-3	0.075(3)	9.6(13)	5.3(9)	0.72(7)	0.40(5)

and high coverages (see Fig. 5). The simulations reproduce qualitatively the large initial drop of the isosteric heats, q_{st}^σ which is typically attributed to a selective adsorption on specific sites of the sample. In our model, the pillars play the role of the strong interacting centers (or acid centers) present in real systems. The plateau region of the isosteric heat is well reproduced, and the simulated curves even develop a small positive slope due to adsorbate-adsorbate interactions (lateral interactions^{51,52}) seen in the experimental isotherm. In Fig. 5 we have plotted the different components of the isosteric heats and one can readily see how the adsorbate-pillar interactions account for the much higher q_{st}^σ values in the first stages of the adsorption process; at intermediate-high loadings the adsorbate-adsorbate interaction is responsible for the rise of the isosteric heat, the adsorbate-wall interaction giving an essentially uniform contribution. In some cases, if the adsorbate-pillar interactions are too strong, this veils the effect of the adsorbate-adsorbate contribution to the total calorimetric isotherm. As a result, q_{st}^σ would exhibit a final plateau or even a drop as the coverage increases before the micropore filling. In the experimental results, the final drop in q_{st}^σ always signals the end of micropore filling.

The adsorption results from the simulations are presented in Table VI, and can be compared to the experimental data of Tables I and II. Notice that considering σ_p as an adjustable

FIG. 4. Experimental and simulated adsorption isotherms of toluene for the sample WYO-3 at 315 K. (a) Volumetric adsorption isotherms. (b) Calorimetric adsorption isotherms.

FIG. 5. Experimental and simulated calorimetric isotherms for toluene on sample WYO-3 at 315 K. Adsorbate-adsorbate (green diamonds), adsorbate-wall (violet triangles up), and adsorbate-pillars (black left triangles) contributions to the isosteric heats are also illustrated.

parameter for each system, allows us to produce simulation results that are consistent with the experiments. The variations of σ_p for different probe molecules are in fact small for each material, usually within 2%–3% reaching up to 6.5% only for then PTS-3 sample. We will present later in the paper a more detailed analysis on the ability of the models to predict the amount of adsorbate that can fill the porous media.

C. Mesitylene adsorption simulations

As we did with toluene, we tuned the energetic parameters, ϵ_w and ϵ_p to attain semiquantitative volumetric and calorimetric isotherms (see Figure 6); and we get $\epsilon_w/k_B \simeq 6$ K, $\epsilon_p/\epsilon_{CH} = 80$, and $\kappa_p = 10.77$ nm⁻¹. The estimates for σ_p are collected in Table V. Notice that the interaction with pillars was considered much more attractive than in the case of toluene. In spite of this, from Figure 6, one sees that the volumetric isotherm from simulations fits well the experimental curve, but the simulated calorimetric isotherm lies at lower isosteric heats than the experimental ones. This situation is reproduced in the fittings of all PILC samples. The very high experimental isosteric heats were also found for mesitylene adsorbed on aluminum-pillared clays by Guil *et al.*³ and

they have been attributed to the presence of strong specific interactions with Al³⁺ in the pillars. It seems that the quantum mechanical nature of these interactions cannot be captured by the somewhat simple interactions of our model, and consequently we have not been able to reproduce the experimental q_{st}^σ without spoiling the volumetric isotherms.

Inspecting the simulation results shown in Fig. 6(a) and even for those pertaining to toluene (Fig. 4(a)), one notices that the size of the error bars is considerable. This is a consequence of the averaging over disorder. Recall that in order to perform these averages 10 different pillar configurations were used, and precisely the dispersion of their respective fractions of accessible space lies at the source of the relatively large errors in the simulated amounts of adsorbate intake.

D. Discussion of simulation results

When comparing all the pillar effective diameters calculated for different probe molecules for a given PILC sample, we observe that they are actually quite similar. One could consider the differences as statistical uncertainties and use a single pillar diameter for all probes, paving the way to have a general model for each of the PILC samples. This first observation, and the fact that the pillar diameters for different samples do not differ much, suggest that our modeling procedure is successful in the determination of reliable estimates of σ_p taking as input the available experimental adsorption results.

A second, and more stringent test of the model and of the assumptions made regarding the distribution of pillars and the accessibility criteria can be achieved by considering for each PILC sample a fixed value of σ_p for different probe molecules, and check whether the model can account for the packing density ratios, d_{pck}/d_{liq} . We have made this test by simulating the adsorption of N₂ and toluene on the different PILC samples. For each PILC sample we considered for both probe molecules the value of σ_p previously obtained in the tuning of the toluene system and the same set of pillar configurations (see Table VII).

Following the procedures described previously we computed the amounts of adsorbate at micropore filling, and taking into account the density of the corresponding bulk liquids

FIG. 6. Adsorption isotherms of mesitylene on sample WYO-3 at 315 K. (a) Volumetric adsorption isotherms. (b) Calorimetric adsorption isotherms.

TABLE VII. Test of the PILCS model, r_{sim} and r_{exp} represent the simulation and experimental results for the ratio of the densities of the toluene inside the pore and in the bulk liquid at the saturation pressure.

Sample	h_p (nm)	ρ_p (nm ⁻²)	σ_p (nm)	$V_{\mu p}$ (cm ³ g ⁻¹)	r_{sim}	r_{exp}
PTS-1	0.71	0.60	0.93	0.093(3)	0.68(9)	0.67
PTS-2	0.70	0.60	0.94	0.084(5)	0.63(11)	0.47
PTS-3	0.70	0.60	0.92	0.101(3)	0.73(8)	0.55
WYO-1	0.85	0.60	0.92	0.104(3)	0.76(7)	0.73
WYO-2	0.85	0.67	0.86	0.098(6)	0.74(10)	0.77
WYO-3	0.78	0.73	0.81	0.100(5)	0.78(8)	1.05

at the saturation pressure we could determine the micropore volume (from the N₂ simulation), and the ratio between the effective density of the toluene inside the porous media (using the previous determination of the micropore volume) and the density of the corresponding liquid phase. In Table VII we show the results of the test. The modeling procedure captures the higher relative density of the toluene at the WYO PILCS, and to some extent the values of the ratios $r = d_{pck}/d_{liq}$. However, it does not provide a quantitative explanation of the whole set of experimental results.

The higher ability of WYO PILCS to host toluene (which is semiquantitatively described by the simulation results—see Table VII) can be better analyzed in the light of the adsorbate density profiles along the z -direction (i.e., the variation of the adsorbate density between the PILC layers). This quantity is plotted for toluene molecules adsorbed in samples PTS-1 ($h_p \simeq 0.70$ nm), WYO-2 ($h_p = 0.85$ nm), and WYO-3 ($h_p = 0.78$ nm) in Figure 7. In graph (a) we have the profiles calculated on the basis of the centers of the aromatic ring and in (b) the profiles obtained from the positions of the methyl groups. One immediately observes that a significant fraction of toluene molecules arrange their ring centers in the intermediate space of the micropore cavity. However, the density of methyl groups has two clear maxima near the walls and it practically vanishes at the center of the micropore. This implies that most molecules with their aromatic ring parallel to the walls are adjacent to the clay sheets, whereas if the aromatic ring of the molecules is about the center of the slit, the ring prefers to be more or less parallel with respect to the z -axis. As the pillar height increases more toluene molecules move towards the center of the pore with their methyl groups pointing to the walls, and the bilayer structure in the inner pore becomes much more pronounced. The most structured profile occurs for WYO-3 sample, leading to a maximum packing of toluene molecules. If one takes a look at the geometry of the toluene molecule (Fig. 2), one realizes that its length is approximately 0.80 nm, which almost exactly fits into the pore height for this sample, 0.78 nm. From an straightforward analysis of the density profile and the molecular geometry one realizes that the molecules organize themselves perpendicular to the pore walls with the methyl groups of adjacent toluene molecules pointing in antiparallel directions. In this way it is possible to approach a maximum packing (partially accounted for in simulations), that it is lost as soon as the molecules have more translational freedom due to entropic effects, as it is seen when comparing the packing

FIG. 7. Density profiles of the toluene molecules adsorbed on various PILC samples at $p/p_0 = 0.31$. The upper graph is calculated on the basis of the aromatic ring centers and the lower graph corresponds to the density profile of the methyl groups.

fractions and density profiles of sample WYO-2 (with larger interlayer separation) and WYO-3.

The precise matching of the pore height and molecular length can thus explain the highest packing fractions of the fluid adsorbed on the WYO-3 sample with the smallest experimental micropore volume, which can be ascribed to the building up of a microscopic structure with some degree of orientational order.

We see from Tables II and VI that the WYO samples exhibit a substantially larger adsorption capacity for mesitylene than the PTS samples. In contrast with the adsorption of toluene, now the WYO-3 sample no longer adsorbs the largest amount of mesitylene, but still, given its small micropore volume, it exhibits the largest packing fraction of adsorbate.

The density profiles for mesitylene adsorption from computer simulation are plotted in Fig. 8 for samples PTS-1, WYO-2, and WYO-3. We observe now that in the case of the WYO-2 sample (the one with the largest pillar height, $h_p = 0.85$ nm), the density profile for the center of mesitylene molecules shows an extra peak with respect to the results found for PTS-1 and WYO-3 samples. The extra peak is located at the center of the slit. Looking at the density profile of methyl groups a peak at the same position appears for WYO-2 sample. Such a peak is absent in samples with shorter pillar heights and also in the density profiles for toluene adsorption.

FIG. 8. Density profiles of the mesitylene molecules adsorbed on a PILC system at $p/p_0 = 0.31$. The density profile depicted in panel (a) shows the positions of the centers of the aromatic rings inside the micropore. In panel (b) it is plotted the density profile of the methyl groups.

Inspection of simulation configurations, together with energy and excluded volume considerations indicate that these central peaks are mainly due to mesitylene molecules with planes perpendicular to the slit walls, with one of the methyl groups pointing to the lower wall, another one pointing to the upper wall, and the remaining one at the center of the slit (see configuration on the right of Fig. 9). The slit width required to accommodate this configuration is, for our model parameters of about 0.86 nm, which is close to the pillar height of the WYO-2 sample, and much larger than the pillar heights

of PTS and WYO-3 samples. The remaining two peaks of the density profile for the center of the rings that are close to the center of the slit can be mainly attributed to configurations of the mesitylene molecules whose aromatic ring is more or less perpendicular to the walls (some tilt might be required for the PTS samples) with two methyl groups adjacent to one of the walls, and the other adjacent to the other wall (middle configurations in Figure 9).

The overall picture of the configurations for mesitylene for micropores with $h_p = 0.78$ nm (WYO-3 sample) is similar to that described in the case of toluene. The molecules oriented as shown in the middle configuration plotted in Figure 9 fit approximately into the pore height, and we are left with a stacking of mesitylene molecules perpendicular to the pore wall, with just a few molecules lying parallel to the walls. This situation corresponds to the maximum packing density (which in the case of toluene was also the maximum of adsorbed quantity). When the pore width shrinks further this stacking no longer prevails, most of the molecules lie parallel to the walls and those that are not parallel have their axis somewhat skewed with respect to the direction perpendicular to the walls. As mentioned before, in all cases, amounts adsorbed are similar, with the sample WYO-3 showing the largest packing.

These results are clearly consistent with the larger molecular size of mesitylene with respect to toluene. Even if the packing effects are not so striking as in the case of toluene, still sample WYO-3 illustrates how the matching of pore width and molecular size leads to the largest packing density.

VI. NEUTRON DIFFRACTION EXPERIMENTS

The neutron diffraction measurements were performed in the SANDALS instrument at the ISIS pulsed neutron scattering and muon spectroscopy facility, Rutherford Appleton Laboratory, U.K.. SANDALS is a time of flight neutron diffractometer with a momentum transfer, Q , spanning from ~ 0.05 to $\sim 50 \text{ \AA}^{-1}$. We used standard TiZr flat sample holders of area $3.5 \times 3.5 \text{ cm}^2$ with a 1 mm gap thickness and 1 mm wall thickness. Previous to the neutron scattering experiments two different samples with the PTS-2 PILC were prepared, namely, a pristine PTS-2 pillared clay and a PTS-2 PILC from the same production batch with a $561.85 \text{ } \mu\text{mol/g}$ uptake of

FIG. 9. Some representative toluene (left) and mesitylene (middle and right) molecular orientations depending on interlayer separation (pillar height). The three horizontal lines in the upper region of the figure mark the three different layer separations of the PILC samples, i.e., 0.71 nm, 0.78 nm, and 0.85 nm.

fully deuterated toluene ($\text{C}_6\text{D}_5\text{-CD}_3$). We opted by the deuterated molecule because protons scatter neutrons incoherently very strongly. At ISIS two sample holders were filled with the corresponding clays within a glove box with inert atmosphere. The beam size was set to $3 \times 3 \text{ cm}^2$ and centered at the sample holder. The total data acquisition time per sample was around 12 h divided in four runs. Data reduction was done using the Gudrun program. Gudrun translates the time of flight spectra to Q spectra, subtracts the container and background signals, corrects for detectors efficiency, normalizes to absolute units using a vanadium measurement and performs all the pertinent corrections (neutron absorption, self-shielding, and multiple scattering).

For an isotropic or orientally averaged sample the neutron diffraction normalized to the number of scatterers can be expressed as

$$F(Q) = \langle \bar{b}^2 \rangle_N + \frac{4\pi\rho}{Q} \int_0^\infty \sin(Qr) r \times (g_{bb}(r) - \langle \bar{b}^2 \rangle_N) dr = \langle \bar{b}^2 \rangle_N + I(Q), \quad (14)$$

where $\langle \dots \rangle_N$ denotes average over the various nuclear species, the bar average over isotopes, and nuclear spin states for each species and b stands for the neutron scattering length. $I(Q)$ is the so-called interference function which tends to zero at large Q 's while $g_{bb}(r)$ is the neutron scattering weighted average of the pair distribution function, that is,

$$g_{bb}(r) = \sum_{\mu, \nu} \bar{b}_\mu \bar{b}_\nu c_\mu c_\nu g_{\mu\nu}(r), \quad (15)$$

where the Greek indexes denote the nuclear species and c_μ is the number concentration for the corresponding species. The pair distribution functions $g_{\mu\nu}(r)$ are the histograms of the corresponding pair distances normalized to that of a uniform distribution. Along with $I(Q)$, $g_{bb}(r)$ is the quantity of our main concern and can be obtained by sine Fourier transform of $QI(Q)$ since

$$d(r) = 4\pi\rho r [g_{bb}(r) - \langle \bar{b}^2 \rangle_N] = \frac{2}{\pi} \int_0^\infty \sin(Qr) QI(Q) dr. \quad (16)$$

The function $d(r)$ is essentially a compact notation for the sine Fourier pair of $QI(Q)$.

The measured diffraction patterns are shown in Fig. 10. The pristine pillared clay shows a rather well defined broad peak at $Q \simeq 0.38 \text{ \AA}^{-1}$ coming from the layered structure and consistent with the X-ray measurements. Such a peak disappears in the toluene loaded sample as a consequence of the diminished scattering length contrast. Instead only a shallow shoulder is discernible in the $0.4\text{--}1 \text{ \AA}^{-1}$ Q -range corresponding to a spatial scale compatible with that expected for the pillars distribution.

The computer simulations required some structural refinement before comparison with the diffraction study. A fully atomistic model for toluene (including explicitly all the hydrogen atoms) and a coarse discretization for the pillars were used while the lamellas remained described as structureless hard walls. The LJ interaction parameters for carbon and hydrogen were taken from the values proposed by Jorgensen *et al.*⁵³ For simplicity, molecules were considered as fully

FIG. 10. Log-Log representation of $I(Q) + 1$ for the PTS-2 pristine pillared clay (solid black) and loaded with toluene (solid blue). (Inset) A zoom of both $I(Q)$'s in a linear scale.

rigid, and no partial charges were included in the model. The calculations of the toluene-pillar correlations were carried out by discretizing the structure of the pillar into eight points, resembling the structure formed by two Zr-tetramers, as explained in Refs. 27 and 28.

The adsorbate-adsorbent potential model considered is basically the same as in the previous simulations, with the only difference that we have considered an additional case in which the toluene-pillar interaction is just described by hard core interactions. Following the same procedure as in the previous simulations the set of parameters (σ_p , ϵ_w , ϵ_p) was tuned to reproduce the experimental adsorption results. From simulations with just hard core toluene-pillar interactions we got $\epsilon_w/k_B = 11.0 \text{ K}$ and $\sigma_p = 0.92 \text{ nm}$. Considering attractive toluene-pillar interactions we got $\sigma_p = 0.94 \text{ nm}$, $\epsilon_w/k_B = 4.0 \text{ K}$, and $\epsilon_p/\epsilon_C = 140$ (where ϵ_C is the potential parameter of the carbon atom⁵³). Paying attention to the case with attractive pillar-toluene interactions, we notice that the value of σ_p obtained with the fully atomistic model is the same as that derived from the AUA model. This is a clear evidence that both models describe toluene molecules with basically the same size.

The molecular configurations required to compute the pair distribution functions, $g_{\mu\nu}(r)$, were extracted from canonical Monte Carlo simulations performed at the saturation densities and at the temperature of the diffraction experiment: $T = 298 \text{ K}$.

In order to favor the comparison between the simulation and diffraction results, we have subtracted the PILC-PILC contribution from the structural data obtained from the experiments. This is easily accomplished, by properly subtracting the $I(Q)$ of the pristine sample to the $I(Q)$ of the loaded sample. As a result, an interference function, $I_{pc}(Q)$, is obtained in which both lamellar-lamellar/lamellar-pillar contributions (not present in our model) and pillar-pillar contributions (omitted in the calculations) are neglected. However, toluene-lamellar contributions, also not included in our model, are unavoidable. At any rate, given the complexity of the lamellas, it seems sensible to try first such a simplified approach. $I_{pc}(Q)$ as well as its $g_{bb}(r)$ counterpart are shown

FIG. 11. The $I(Q)_{ipc}$ function (solid blue). The inset show the corresponding $g_{bb}(r)$ (solid blue) as well as the calculated $g_{bb}(r)$ for a model with pillars of 0.92 nm diameter and pure steric molecule/pillar interaction (dashed red line).

in Fig. 11. In practical terms $g_{bb}(r)$ has been obtained through Eq. (15) but restricting the Q -range up to $Q_c = 13.5 \text{ \AA}^{-1}$ using the Lorch prescription.⁵⁴ Such a procedure comes as a consequence of the statistical noise in $QI(Q)_{ipc}$ which becomes the most relevant contribution above Q_c . The Lorch prescription consists in a multiplication of the restricted $QI(Q)_{ipc}$ by a $\text{sinc}(Q)$ function with its first zero at Q_c in order to smooth out the ripples introduced in $d(r)$ by the sudden termination of its Fourier pair. As a counterpart, the resolution in $d(r)$ is limited to $\sim \pi/Q_c$.

In order to calculate the $g_{bb}(r)$ distribution from the simulation data we need to assign a scattering length, $\bar{b}_p$, to the discretized pillar scattering centers. Since the composition of the pillars depends on not well-known details of the PILC synthesis process, we have left $\bar{b}_p$ as an adjustable parameter. With sufficiently high values of $\bar{b}_p$, certainly the negative peak is reproduced. However, we need some reference value to compare with to avoid unphysically high values of $\bar{b}_p$. Probably, the structural possibility amounting for the highest $\bar{b}_p$ value is a pure monoclinic ZrO_2 pillar as assumed in Ref. 28. As

shown in the following results, our final $\bar{b}_p$'s are well below such a reference (denoted by $\bar{b}_{\text{ZrO}_2}$).

The result for a 0.92 nm pillar diameter, $\bar{b}_p = 1.19$ ($\bar{b}_{\text{ZrO}_2} = 2.97$), and pure steric interactions between molecules and pillars is shown in the inset of Fig. 11. Taking into account that our simple model does not include toluene-lamella distances the qualitative agreement is really satisfactory. This makes us confident that we have properly subtracted the pristine pillared clay interference function. However, the real space representation encoded in $g_{bb}(r)$ is very suitable for short range spatial scales but not for the intermediate scales corresponding to the pillar distribution. By sine Fourier transform of the calculated $d(r)$ we come back to the reciprocal space by means of Eq. (15). The results are summarized in Fig. 12.

The first thing to comment in regarding the $I(Q)_{ipc}$ modeling is that the negative peak comes as a consequence of the relevance of the toluene-pillars cross-correlations. Since under our adsorption conditions the microporosity should be filled with toluene, the form factors of the toluene and pillars distributions should be at these intermediate length scales approximately one the negative of the other. As a consequence, the cross-term, i.e., the product of both form factors should be similar to the negative of the squared modulus of one of them while the rest of possible contributions are all positive. As expected, for a sufficiently strong value of b_p the negative peak develops in the model $I(Q)_{ipc}$. In Fig. 12(a) the $I_{ipc}(Q)$'s corresponding to the measured and the model $g_{bb}(r)$ shown in the previous figure are represented. The overall oscillations of the model $I_{ipc}(Q)$ matches those of the sample (b_p as well as an overall scaling factor has been chosen to reinforce such a comparison) but it fails by a substantial amount in the positions of the main minima and first maxima. At a first glance, the obvious implication is that the pillar diameter should be larger. We have explored such a possibility through a coarse approximation in which the toluene molecular distribution is approximated by a slab of constant b with embedded cylinders of a distinct constant scattering length density (only the contrast between the two b densities matters) representing

FIG. 12. A comparison of the measured $I_{ipc}(Q)$ and several model calculations. The solid blue line represents the measured $I_{ipc}(Q)$ in both panels. The red solid lines are the results for a numerical model with 0.92 nm pillar diameter, $\bar{b}_p = 1.19$ and steric molecule/pillar interactions (a) and with 0.94 nm pillar diameter, $\bar{b}_p = 1.24$, and attractive molecule/pillar interactions (b). The black dashed lines are the coarse-grained calculations explained in the text matching the pillar diameters and concentration of the corresponding numerical models. The black dotted line in the (a) panel is the coarse-grained calculation with a 1.3 nm pillar diameter.

the pillars. In a first approximation, the orientational average is assumed uncorrelated with the spatial distribution. Under such conditions, $I_{ipc}(Q)$ can be approximated by the negative of the adequate hard disks structure factor multiplied by the squared modulus of a cylinder form factor of suitable height and diameter.⁵⁵ As can be seen in Fig. 12(a), it departs significantly from its numerical counterpart with a first maxima shifted towards lower Q 's. At any rate, it serves to gauge the diameter value to match the sample $I(Q)_{ipc}$. Indeed, it can reproduce quite well the overall peak structure but at the expense of much higher diameter values (around 1.3 nm) than those extracted from previous adsorption analysis. As mentioned, our accessibility analysis is dependent on the number density of pillars estimated under the assumption of zirconium tetramers as intercalating species²⁶ by which a different composition of the intercalates could imply a different pillar density. This could well lead to somewhat larger pillar diameters, but in any case an increase by a 40% in diameter seems unreasonably high.

The dilemma can be solved by taking into account that the diffraction signal is also modulated by the peak coming from the layered lamellar structure acting as a structure factor. Unfortunately, the peak is narrow enough to dominate the overall shape of the minima and the turning point of the first maxima. Notice that such a modulation is intrinsic to the system. Whatever we would do to enhance the contrast of the pillars will also enhance the contrast of the layered structure peak. As a consequence it is clear that a far more detailed model is needed if we want to fully exploit the information content of the neutron diffraction data. Within this respect, the result shown in Fig. 12(b) is quite interesting. There, the numerical model refers to pillars of 0.94 nm in diameter and $\bar{b}_p = 1.24$ ($\bar{b}_{ZrO_2} = 3.11$) with the attractive molecule/pillar interaction favored in the adsorption calculations presented in Secs. V A–V D. As it can be seen, the model $I_{ipc}(Q)$ clearly discriminate between the two types of interaction pointing in this case towards the pure steric interaction. Obviously, at this stage this result cannot be taken as an evidence in favor such an interaction. Its real value comes from the clarity of the discrimination, a non-trivial expectation completely neglected in the coarse approximation. It increases our confidence in that the efforts necessary to develop a more complete model could well be profitable.

VII. CONCLUSIONS

In summary, we have presented a rather comprehensive study of the volumetric and microcalorimetric adsorption of toluene and mesitylene in various PILC samples by means of extensive computer Monte Carlo compared with experimental adsorption measurements and complemented by neutron scattering experiments. Despite the crude approximations of the PILC model, in which both the internal layer and pillar atomic structures are neglected, and with a pillar distribution that only contains accounts for steric effects between pillars and disregards further potential interpillar correlations, the model provides a reasonable explanation of the larger adsorption capabilities of certain samples (WYO), and the peculiar high density effective packing of toluene in the WYO-3

sample, in terms of the matching of the interlayer spacing to the molecular size of toluene, and to a lesser extent mesitylene molecules. From the analysis of the neutron scattering, one might interpret that the effective attractive interactions resulting from the fit to adsorption data are somewhat overestimated, but if one wants to go beyond a very rough qualitative comparison, a much more detailed atomistic description of the PILC layers and pillars is absolutely required. This, together with a more comprehensive neutron scattering study of a series of probe molecules will be the subject of future work.

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