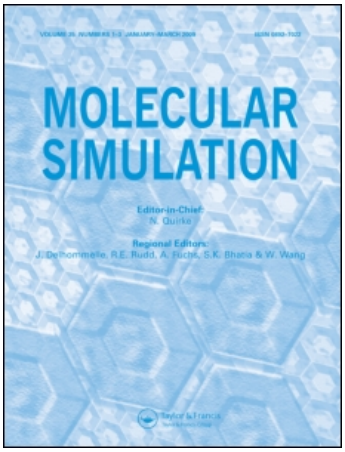

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Adsorption/Condensation of Xenon in a Disordered Silica Glass Having a Mixed (Micro a Mixed and Meso) Porosity

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ADSORPTION/CONDENSATION OF XENON IN A DISORDERED SILICA GLASS HAVING A MIXED (MICRO A MIXED AND MESO) POROSITY

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We have studied adsorption of xenon in a mixed (micro and meso) porosity silica controlled porous glass (CPG) by means of grand canonical Monte-Carlo (GCMC) simulation. A numerical sample of the CPG adsorbent has been obtained by using an off-lattice reconstruction method recently introduced to reproduce topological and morphological properties of correlated disordered mesoporous materials. The off-lattice functional of ($100\,m^2/g$)-Vycor is applied to a simulation box containing silicon and oxygen atoms of orthorhombic silicalite zeolite with an homothetic reduction of factor 2.5 so as to obtain a CPG sample exhibiting both micro and meso porosity. A realistic surface chemistry is then obtained by saturating all oxygen dangling bonds in the mesoporosity with hydrogen. The Xe adsorption/desorption isotherms is calculated at 195 K. It is shown that in the particular case of xenon, the difference of energetics between zeolitic micropores and CPG mesopores lead to two distinct adsorption processes which occur consecutively. As a consequence, both the microporosity and the mesoporosity can be calculated independently.

Keywords: Controlled porous glass; Vycor; Xenon; Adsorption

INTRODUCTION

The vast majority of mesoporous materials are disordered structures. Silica controlled porous glasses (CPG) constitute a large class of materials among which is Vycor, a porous silica glass widely used as a model structure to study the properties of confined fluids. In fact, there are two kinds of vycor (it is usually

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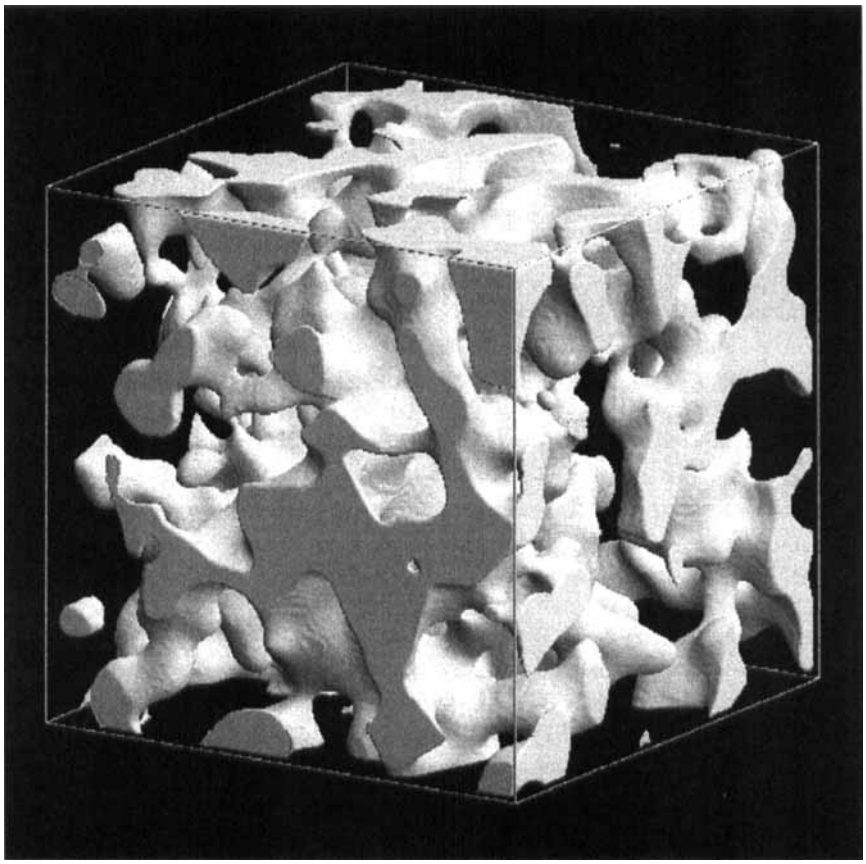

FIGURE 1 A numerical reconstruction of ($100\,m^2/g$)-vycor. The box size is 100 nm. One sees through the silica matrix, the porosity in grey.

referred to as Vycor-7930 by the manufacturer Corning): a first type with a specific surface area around $100\,m^2/g$ and a second at around $200\,m^2/g$ (see Fig. 1). The pores in the low-specific-surface-vycor have an average radius of about 35–40 Å (assuming a cylindrical geometry) [1]. Conversely, for the high specific-surface material, the mean pore radius is around 20–25 Å [2]. Although being a disordered material having a rough inner interface [3], Vycor is also known to exhibit no real microporosity (i.e. pores of a few molecular diameter large; mesopores are pores having a mean diameter larger that 2 nm). However CPGs can exhibit microporosity depending on synthesis conditions and chemical and heat treatments. Consequently, the difference between the concept of surface roughness and microporosity is small: the core matrix of a mesoporous solid

limited by a rough interface with a typical characteristic length on the order of a few nanometers can be considered as containing some microporosity.

It is known from theoretical and simulation studies on simple pore geometries (slits and cylinders) that confinement strongly influences the thermodynamics of confined fluid [4]. The effect of the matrix disorder in terms of pore morphology—the pore size and shape- and topology, the way the pores distribute and connect in space—on the thermodynamics of confined molecular fluid still remain to be clarified. This first raises the challenge of describing the morphology and the topology of these porous solids [3]. The aim of this work is to provide an insight in the adsorption mechanism of a simple adsorbate (xenon) confined in a mixed porosity disordered and connected medium at a microscopic level using a molecular simulation technique such as the grand canonical Monte-Carlo method (GCMC).

This paper is organized as it follows. The second section presents the numerical reconstruction method and the GCMC method used here to simulate the adsorption/desorption process. The third section presents some results in the case of xenon at 195 K. In the last section, some conclusions are given and a characterization technique of mixed porosity material is presented.

COMPUTATIONAL DETAILS

Generating a Mixed Porosity Solid

First we start by using an off-lattice reconstruction algorithm in order to numerically generate a mesoporous structure which has the main morphological and topological properties of real (low-specific surface area 100 m^2/g) vycor in terms of pore shape: close inspection of molecular self-diffusion shows that the off-lattice reconstruction procedure allows to reproduce many properties such as tortuosity, and in and out-pore two-point correlation functions (see Fig. 1) [3]. In agreement with the experiment, the small angle scattering spectrum of the numerically reconstructed vycor shows a correlation peak which corresponds to a minimal (pseudo) unit-cell size around 270 Å [1]; a simulation box cell with this size is too large to be correctly handled in an *atomistic* Monte-Carlo simulation of adsorption in a reasonable amount of CPU time. This is the reason why we have applied homothetic reduction with a factor of 2.5. This transformation preserves the mesopore morphology but reduces the average pore size from 70–90 Å to roughly 30–35 Å [5]. Interestingly enough, the numerical pseudo-vycor purely mesoporous sample has both a specific surface area and an average pore size close to that of the real high specific surface area vycor (around 200 m^2/g) [6,7].

An atomistic description of a mixed (meso and micro) porosity solid can be obtained by applying the off-lattice functional to a box containing the silicon and oxygen atoms of $5 \times 5 \times 7$ unit cells of orthorhombic silicalite, a purely siliceous zeolite [8] (the simulation cell volume is roughly 100^3 Å^3). The off-lattice functional represents the Gaussian field associated to the volume autocorrelation function of the studied porous structure [3]; it allows cutting out portions of the initial volume in order to create in our case, the mesoporosity of the resulting structure (assuming a mesoporosity at $\phi_{meso} = 30\%$ which corresponds to that of many silica porous glasses including Vycor). Note that this approach encompasses a statistical description: it allows generating a set of morphologically and topologically equivalent numerical samples of pseudo-vycor. Periodic boundary conditions are applied in order to simplify the GCMC adsorption procedure. An example of a pure mesoporous pseudo-vycor is given in Fig. 2.

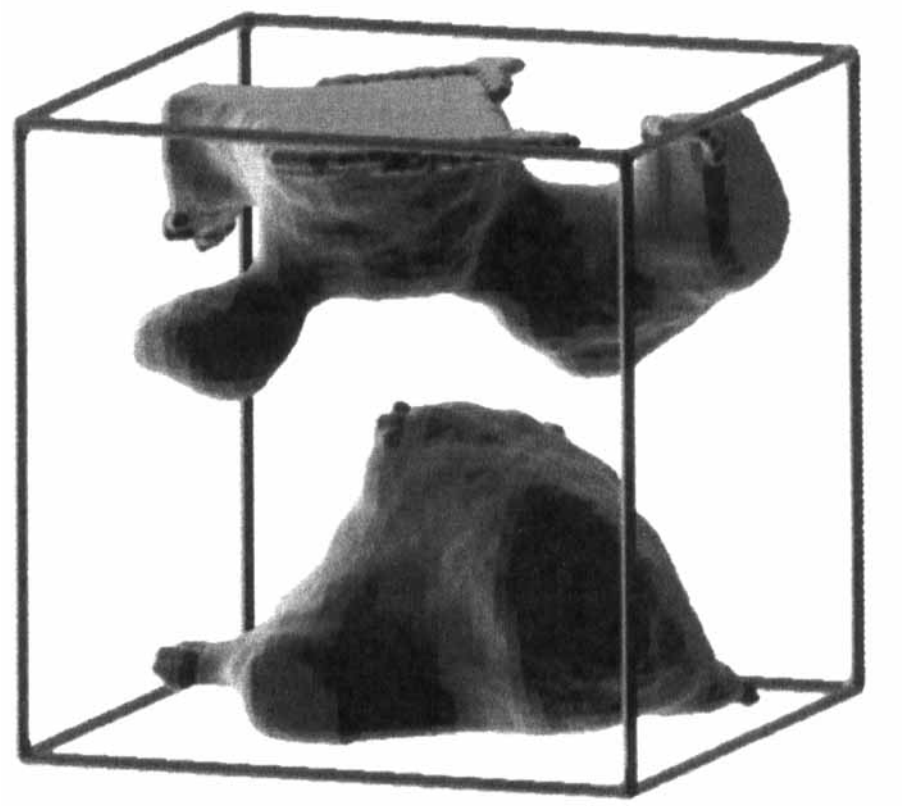

FIGURE 2 A typical sample of the mesoporosity of the mixed-porosity numerical sample. The box size is around 10 nm. One sees through the silica matrix, the porosity in grey.

In order to model the mesopore inner surface in a realistic way and to ensure electroneutrality, all oxygen dangling bonds are saturated with hydrogen atoms (all silicon atoms in an incomplete tetrahedral environment are also removed). The gradient of the local gaussian field allows to place each hydrogen atom in the pore void perpendicular to the interface at 1 Å from the closest unsaturated oxygen: the density of OH group per unit area is very close to that found experimentally (7–8 OH groups per nm^2). We have demonstrated in a previous publication [5] that this procedure allows a good description of the surface roughness and chemistry of silica mesoporous glasses. Our numerical sample thus contains both some *micro* and some *meso* porosity. Obviously the resulting value of the total porosity is not any more that of a pure mesoporous glass since the matrix contains zeolitic silicalite-like microporosity. One can then consider our mixed numerical structure as a defective silicalite crystal having mesoporous cracks. This may not be far from the reality since hysteretic adsorption isotherms (characteristics of mesoporosity; see below) have been found experimentally in the case of adsorption of nitrogen in silicalite [9].

The Grand Ensemble Monte-Carlo Simulation Technique as Applied to Adsorption

In this work, we have used a PN-TrAZ potential function as reported for adsorption of xenon in silicalite (a purely siliceous zeolite): it is based on the usual partition of the adsorption intermolecular energy which can be written as the sum of a dispersion interaction term with the repulsive short range contribution and an induction term (no electrostatic interaction in the rare gas/surface intermolecular potential function) [10]. The dispersion and induction parts in the Xe/H potential is obtained assuming that hydrogen atoms have a partial charge of $0.5e$ ($q_O = -1e$ and $q_{Si} = -2e$, respectively) and a polarizability of 0.58 $Å^3$; the Xe/H repulsive contribution is adjusted on the experimental (Vycor) low coverage isosteric heat of adsorption (Qst(0) = 17 kJ/mol) [11]. One may infer that the isosteric heat of adsorption at zero coverage on a purely mesoporous pseudo-vycor numerical sample should be higher than that measured on the real material due to higher surface curvature induced by the homothetic reduction. In fact, Qst(0) does not depend strongly upon surface curvature for pore larger than 8 Å in size: in the case of the Xe/silicalite system at 121 K (pore diameter 5 Å), Qst(0) = 27.4 kJ/mol [10], it decreases to 17.9 kJ/mol in the cavity of NaY zeolite (pore diameter 8 Å) [12]. Note that in the last case, Qst(0) is only 1 kJ/mol larger than that in Vycor. Therefore, we can safely consider that the isosteric heat of adsorption at zero

coverage in a non microporous numerical pseudo-vycor samples is that of the real material [5]. Obviously, we expect that the isosteric heat of adsorption in the microporosity will be close to that found for the pure zeolite case [10]. The Xe/Xe potential energy was calculated on the basis of a Lennard–Jones function ($\varepsilon = 281$ K and $\sigma = 3.89$ Å) which gives a good fit of the "true" two-body Xe/Xe potential [13]; the corresponding bulk saturating pressure is then 65,000 Pa at 195 K [14].

In the Grand Canonical Ensemble, the independent variables are the chemical potential, the temperature and the volume [15]. At equilibrium, the chemical potential of the adsorbed phase equals that of the bulk phase, which constitutes an infinite reservoir of particles at constant temperature. The chemical potential of the bulk phase can be related to the temperature and the bulk pressure. Consequently, the independent variables in a GCMC simulation of adsorption in Vycor are the temperature, the pressure of the bulk gas and the volume of the simulation cell containing the porous sample as defined above. The adsorption isotherm can be readily obtained from such a simulation technique by evaluating the ensemble average of the number of adsorbate molecules. Note that the bulk gas is assumed to obey the ideal gas law. Control charts in the form of plots of a number of adsorbed molecules and internal energy versus the number of Monte-Carlo steps were used to monitor the approach to equilibrium. Acceptance rates for creation or destruction were also followed and should be equal at equilibrium. After equilibrium has been reached, all averages were reset and calculated over several millions of configurations (3×10^5 Monte-Carlo steps per adsorbed molecules). In order to accelerate GCMC simulation runs, we have used a grid-interpolation procedure in which the simulation box volume is split into a collection of voxells [16]. The Xe/Vycor adsorption potential energy is calculated at each corner of each elementary cubes. A cut through a grid is presented in Fig. 3. Such a grid can also be used to obtain the porosity and specific surface [6,7]. We have found an average specific surface due to the mesoporosity at around 220 m^2/g. The nominal specific surface area of silicalite being at around 400 m^2/g [17], then the total specific surface area of the mixed porosity material is at around $(0.7 \times 400) + (0.3 \times 220) = 345\ m^2/g$. Thus the addition of a microporosity to the original mesoporous material leads to a very large increase of the specific surface area.

RESULT AND DISCUSSION

We first consider in this study the adsorption of Xe in silicalite zeolite [16]. Figure 4 shows the GCMC adsorption isotherm of Xe in silicalite at 195 K

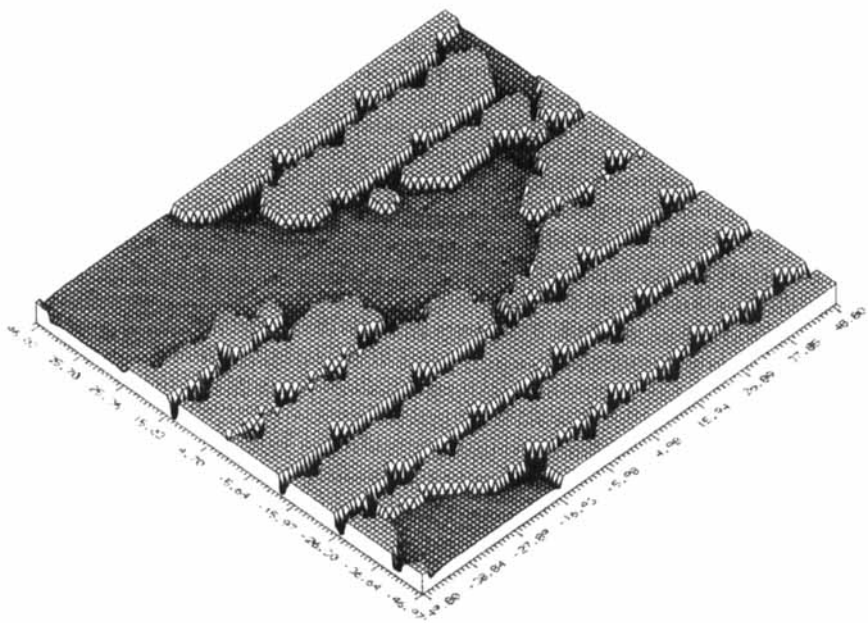

FIGURE 3 A 2D energy grid map. The two in-plane dimensions are x and y space dimensions (in Å) while the third dimension is the adsorbate/matrix potential energy. Darkest area correspond to lowest adsorbate/matrix potential energy sites. One can distinguish between the microporosity and the mesoporosity. In the mesoporosity, adsorption sites are located near to the interface in the regions of large curvature. In the microporosity, the adsorption sites can be identified in the zeolitic channels at well defined locations.

obtained with the adsorbate/zeolite potential presented above. The adsorption isotherm is reversible and characteristic of the microporous solids (type I in the IUPAC classification [18]). Note that in the case of adsorption in silicalite, there is no adsorbate/hydrogen interaction to consider since silicalite is a pure silica structure. It is important to note that the adsorbate/matrix potential used through out this work is the same as far as oxygen and silicon species are concerned. A statistical sampling of the porosity of silicalite obtained by probing the adsorbate/silicalite potential energy grid, gives a porosity in the case of Xe at around $\phi_{\text{silicalite}} = 12.4\%$. The maximum adsorbed amount is around 16 Xe/unit cell: this corresponds to a density of 0.0240 Xe/Å^3 The xenon adsorbed phase in silicalite is much denser than that in the liquid bulk phase at the same temperature (0.0129 Xe/Å^3) [5–7]. This effect was also observed in the case of argon confined in silicalite at 77 K [19]: 0.0467 Ar/Å^3 (in-silicalite confined), 0.0232 Ar/Å^3 (bulk solid). The simulated isotherm is in good agreement with experimental data [16].

Figure 5 presents the isosteric heat versus loading curve so-called isosteric heat curve in the remainder of this paper. As already discussed in Ref. [16], this curve

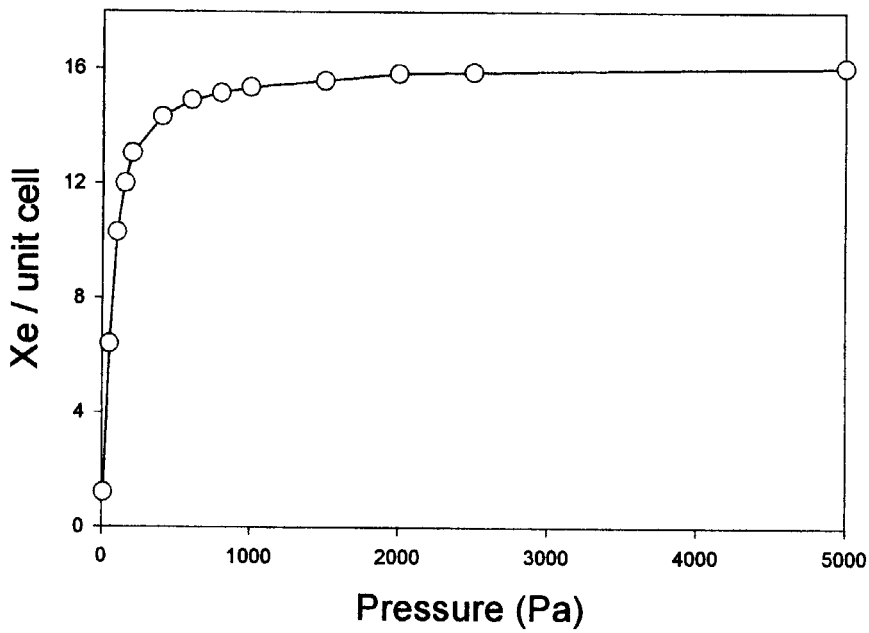

FIGURE 4 Adsorption of xenon in silicalite at 195 K.

is characteristic of adsorption on an energetically homogeneous hypersurface of potential energy: the adsorbate/zeolite contribution remains constant as loading increases. The total isosteric heat being the sum of the adsorbate/adsorbate and the adsorbate/surface terms, is then an increasing function of loading since the adsorbate/adsorbate contribution also increases with loading. However, one can note that at loading corresponding to 16 Xe/unit cell, the total isosteric heat curve presents a decrease which allows to locate the maximum amount that can be adsorbed in silicalite zeolite. These features on the isosteric heat curve have also been reported for Xe and methane adsorption in NaY zeolite [12].

The second step is to consider adsorption in a purely mesoporous silica as reported in a series of paper by different authors [4,5,20–25]. Figure 6 shows the GCMC adsorption/desorption isotherm at 195 K in a purely mesoporous silica as obtained from the off-lattice method (see above). This isotherm presents a hysteresis loop corresponding to the capillary gas–liquid transition characteristic of mesoporous structure. Interestingly enough, at low pressure, one can see that the adsorption isotherm is nearly linear with increasing pressure and can be classified as being of type III in the IUPAC classification [18]. Snapshot analysis has revealed that xenon does not "wet" the inner surface of such mesoporous solids [5]. Although at the very first step of the adsorption process, Xe adsorbs in

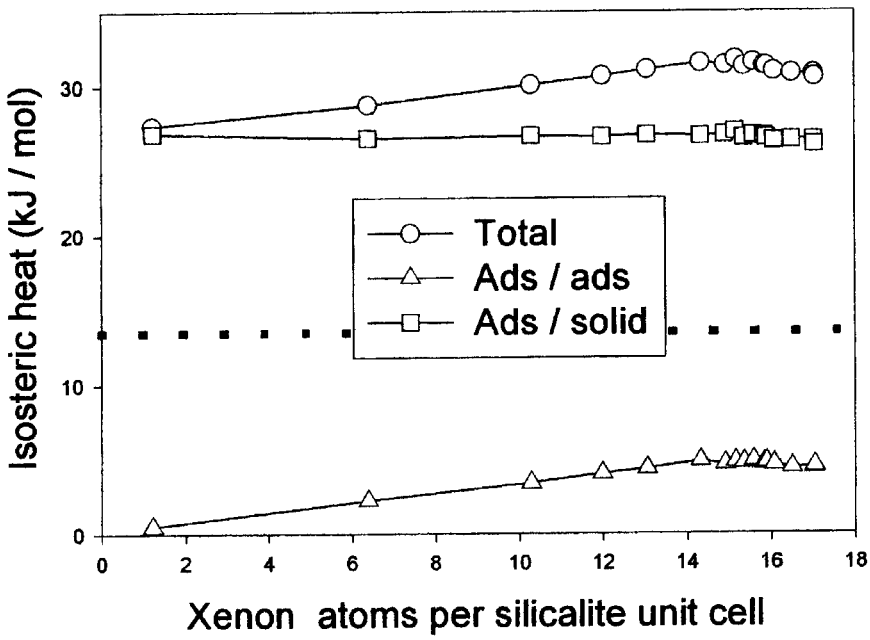

FIGURE 5 Isosteric heat versus loading curve for the Xe/silicalite system at 195 K. Its two contributions (ads/ads and ads/solid) are also shown. The horizontal dashed line indicates the value of the heat of liquefaction of bulk xenon (13.5 kJ/mol).

the primary adsorption sites of lower potential energy, incoming adsorbed molecules tend to aggregate with molecules already adsorbed to form clusters (or droplets) located in the regions of space of higher (local) curvature. A further analysis of such an adsorption process has shown that the specific surface area as measured from xenon adsorption isotherm at 195 K was underestimated by a factor of two compared to the geometrical value obtained from the chord length distribution [6,7,24] in agreement with experiment on real disordered silica mesoporous solids.

Figure 7 presents the corresponding isosteric heat curve. One can see that it is characteristic of adsorption in an energetically heterogeneous environment: the decrease of the isosteric heat as loading increases is due to the decrease of the adsorbate/silica contribution; the adsorbate/adsorbate being of course an increasing function of loading. One can explain this on the basis of the energetic heterogeneity in the system due to local roughness (on the scale of a nanometer) and the collection of surface curvatures due topological and morphological disorder of the pore network inherent to this kind of porous material. We note that there is a large energy contrast between xenon adsorption in silicalite and that in

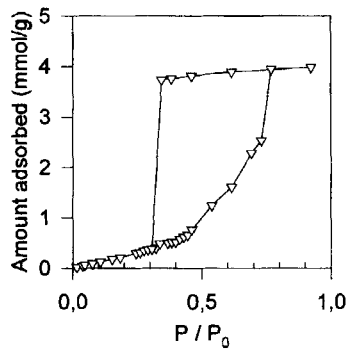

FIGURE 6 Adsorption of xenon in a purely-mesoporous pseudo-vycor system at 195 K.

disordered porous silica glass. As usually obtained in experiment, the total isosteric heat tends to the value of the liquifaction enthalpy (13.5 kJ/mol for xenon).

The third step in this study was to consider a mixed porosity system having both a microporous and a mesoporous contribution as obtained from the off-lattice method presented above and applied to a simulation box originally containing $5 \times 5 \times 7$ unit cells of orthorhombic silicalite ($a = 20.07$ Å, $b = 19.92$ Å, $c = 13.42$ Å, $V_{\text{silicalite}} = abc$) [8]. Figure 8 presents the adsorption/desorption isotherm at 195 K on such a mixed porosity material. One can see that this curve still exhibits the hysteresis phenomenon characteristic of capillary condensation. We shall come back to this point later. Interestingly, one can see that in the low pressure domain, the shape of the adsorption isotherm of the mixed porosity material closely resembles the pure zeolite material (see Fig. 4). This is indeed due the presence of microporosity embodied in the core of this essentially mesoporous material. The density of the matrix was evaluated at 1.249 g/cm^3 which corresponds to a mesoporosity at $\phi_{\text{meso}} = 30\%$ ($\rho_{\text{mixed}} = 0.3 \times \rho_{\text{silicalite}}$; $\rho_{\text{silicalite}} = 1.785$ g/cm^3 [8]). However, if we now compare the density of the mixed material to that of non-porous silica ($\rho_{\text{silicalite}} = 2.15$ g/cm^3), one finds that the mixed material has a porosity at 42%.

Figure 9 presents the corresponding isosteric heat curve. One can distinguish two regions. The first corresponds to adsorption within the microporosity. Indeed, we can see that the shape of the isosteric heat curve has the same shape as that obtained in the case of adsorption in pure silicalite (see Fig. 5). In particular, one can identify the maximum amount adsorbed in the microporosity by locating the abrupt decrease at around 1900 Xe in the simulation box. This corresponds to a density of 0.0234 Xe/Å^3 (very close to that found in the case of xenon adsorption in pure silicalite at the same temperature). This value of density is obtained by

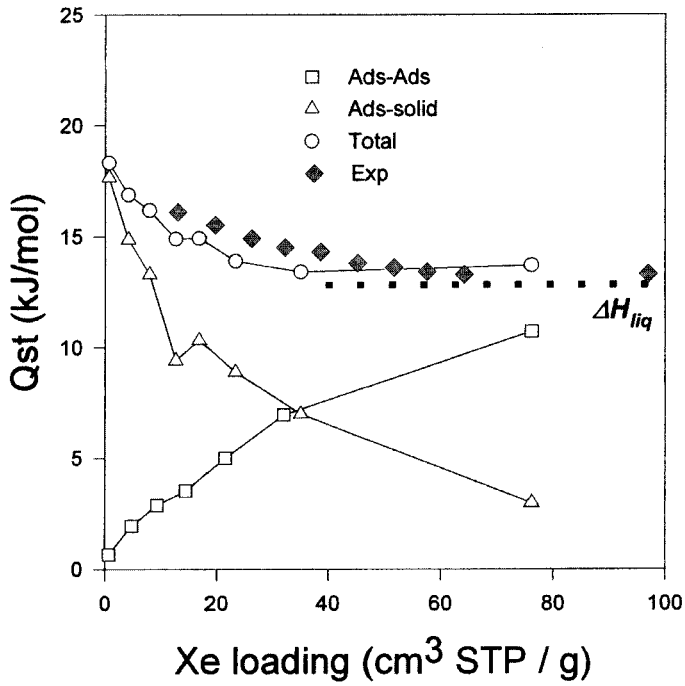

FIGURE 7 Isosteric heat versus loading curve for the Xe/pseudo-vycor system at 195 K. Its two contributions (ads/ads and ads/solid) are also shown. Experimental data are from Ref. [11]. The horizontal dashed line indicates the value of the heat of liquefaction of bulk xenon (13.5 kJ/mol).

multiplying the total simulation box volume (938,917 Å^3) by the factor $[\phi_{\text{silicalite}}(1 - \phi_{\text{meso}})]$ so as to have the microporous volume of our numerical mixed porosity sample (81,207 Å^3). Therefore, we infer that the analysis of the isosteric heat curve of a mixed porosity material is an efficient tool to calculate a microporous volume. This method is especially valid when the contrast of energetics between adsorption processes in the micro and meso-porosities is large as it is in the case of xenon. The low-pressure snapshot presented in Fig. 10a does indeed confirm the xenon adsorption mechanism: the vast majority of the xenon atoms are adsorbed in the microporous channels of silicalite; there are very few xenon atoms adsorbed in the vicinity of the micropore openings (connections to mesoporous domains). In the case of argon, the isosteric heat of adsorption at 77 K is 14.5 kJ/mol when adsorbed in silicalite [10] while it is around 13 kJ/mol in mesoporous silica [25]. Therefore one expects that adsorption in the microporosity and in the mesoporosity will occur at the same time. As a consequence, the isosteric heat curve will not distinguish between these two processes. Interestingly enough, the amount adsorbed necessary to fill the

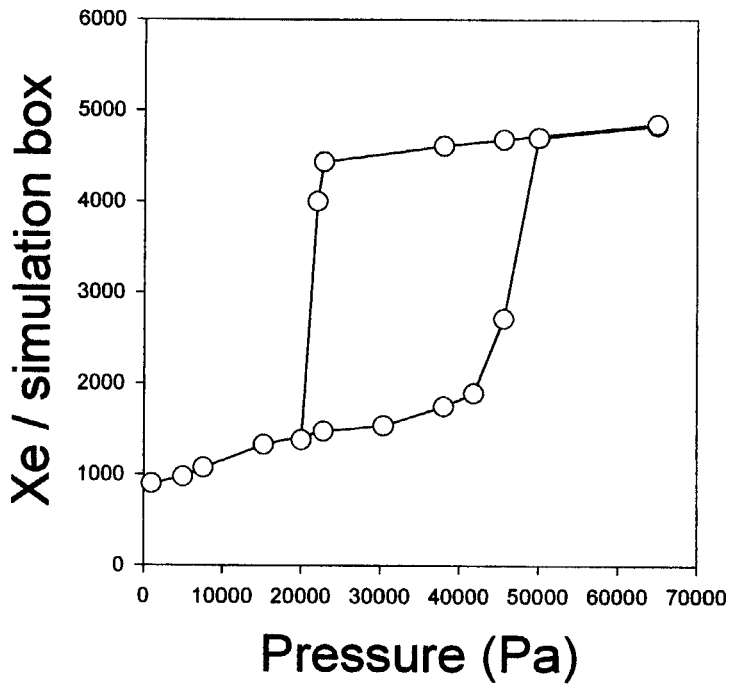

FIGURE 8 Adsorption of xenon in the mixed porosity system at 195 K.

microporosity, is reached just before the beginning of the in-mesopore capillary condensation confirming that in the case of xenon there is no adsorbate film formation inside the mesoporosity; xenon gradually condensates in the higher curvature places of the mesoporous interface (see Fig. 10b and c).

The ratio between the volume corresponding to the microporous volume of the mixed material with that of silicalite ($\phi_{\text{silicalite}} V_{\text{silicalite}}$) is 78.7. Thus multiplying the original Xe/silicalite isotherm by this value, one obtains the microporosity contribution to the total isotherm of the mixed material. The addition of such a contribution to the pure mesoporous isotherm gives a composed isotherm shown in Fig. 11, which is in good agreement to that directly obtained from GCMC calculations for the mixed material. This further demonstrates that in the case of xenon, adsorption and condensation proceed in two distinct steps (i) the microporous filling (ii) adsorption and condensation in the mesoporosity. The adsorption of Xe at 195 K thus seems to provide an interesting method which allows to distinguish between micro and porosity. We further stress that it may not be applicable to other simple usual gases such as argon or nitrogen at 77 K since the contrast of energetics between the two processes may not be sufficient.

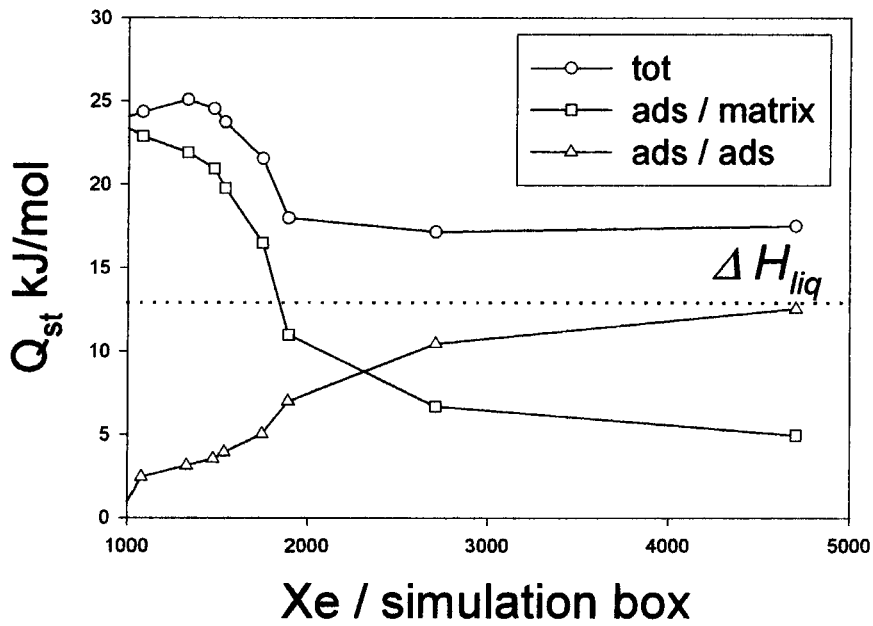

FIGURE 9 Isosteric heat versus loading curve for the Xe adsorbed in the mixed-porosity system at 195 K. Its two contributions (ads/ads and ads/solid) are also shown. The horizontal dashed line indicates the value of the heat of liquefaction of bulk xenon (13.5 kJ/mol).

Let us turn now to the hysteresis phenomenon as observed for both the pure mesoporous and the mixed porosity materials. Capillary condensation is often seen as a first order transition: theoretical and simulation studies have demonstrated that it is indeed the case for simple pore geometries (slits and cylinders) where no disorder is present (neither in terms of pore morphology nor in terms of network topology). However, in disordered systems, the possibility of having no first order phase transition is now considered in some cases (even for adsorption/desorption isotherms presenting the hysteresis phenomenon): due to the collection of different curvatures, the system tries to connect a large number of metastable states (of roughly the same grand free energy) avoiding phase coexistence [26]. The hysteresis loop as seen experimentally does have however the usual behavior with temperature: it shrinks and disappears at a temperature that we can define as a pseudo or apparent critical temperature [25]. If one postulates that there is indeed a pore critical point, then at constant temperature, a confined fluid will be supercritical in small pores and there will be a pore critical size above which the fluid remains subcritical. In terms of confinement, we can thus consider a fluid confined in a zeolitic microporous network to be supercritical (having large density fluctuations). If a given mesopore is connected

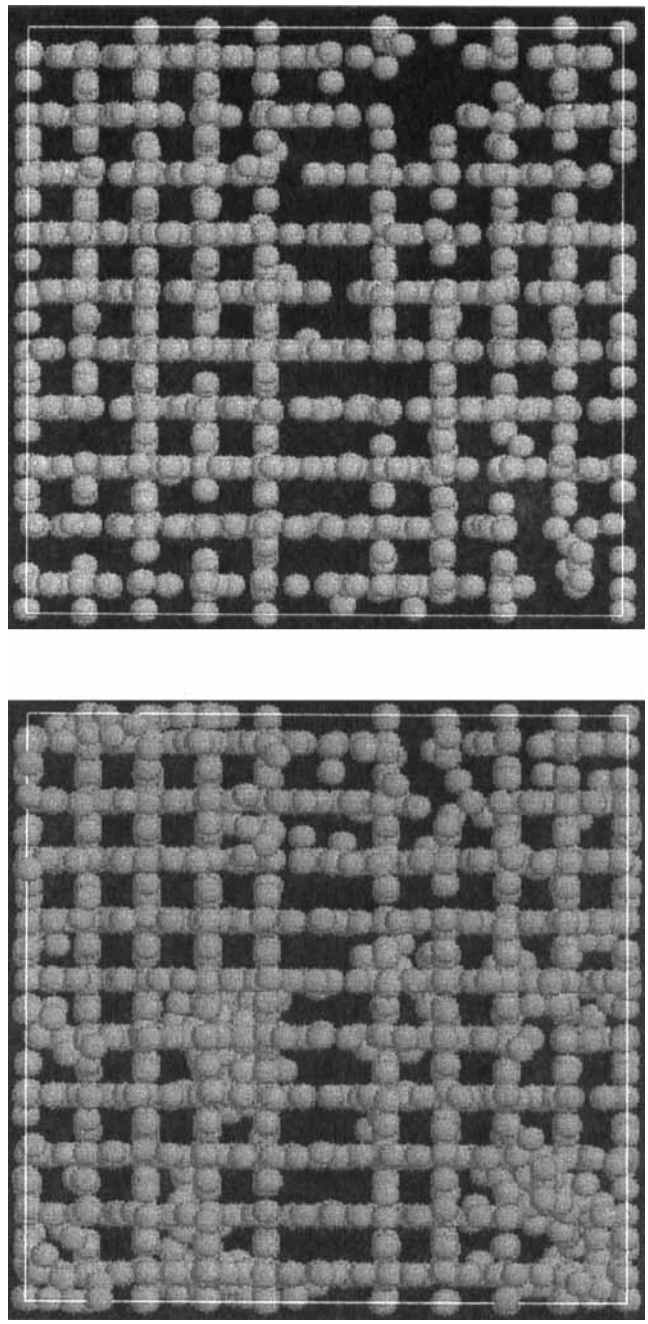

FIGURE 10 *caption opposite*

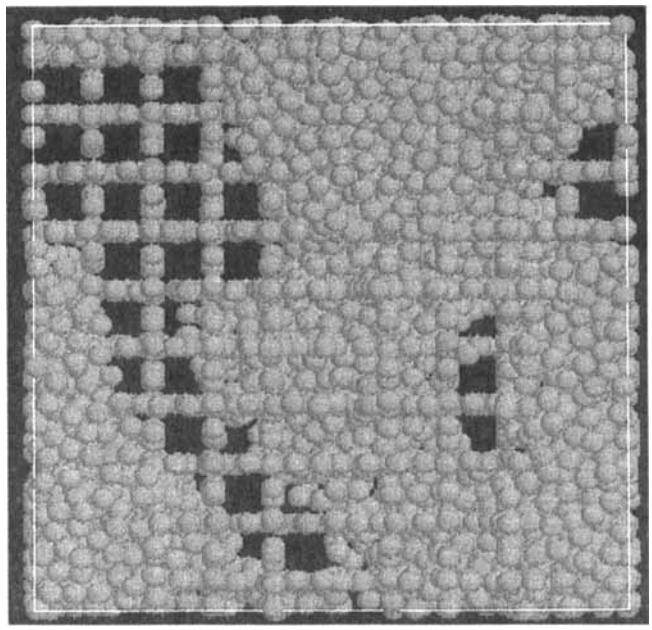

FIGURE 10 Xe adsorbed phase (x, y) snapshot at (a) low pressure; (b) just before capillary condensation and (c) at mesopore completion.

to another one through some micropores, diffusion between mesopores can always be achieved, thanks to the micropores since there will be no gas–liquid interface. In other words, a given mesopore can always empty through smaller pores filled with supercritical fluid. However, the critical property of such confined fluid may not show up because in such a confining environment, the fluid/solid interaction entirely triggers the adsorption mechanism: the thermodynamics, the dynamics and the structure of the adsorbed phase are dominated by such a contribution to the total energy (even in the high loading regime). As shown in Fig. 8, the presence of an hysteresis loop in the adsorption/desorption isotherm, does seem to indicate that a simple fluid such as xenon confined in the mesoporosity of mixed porosity material is still undercritical: the microporosity does not influence the capillary phenomenon occurring in the mesoporosity.

Monson and Sarkisov [22] have demonstrated that the GCMC approach to adsorption and desorption processes are strictly equivalent to brutal force (dual controlled volume) molecular dynamics (GCMD): adsorption/desorption isotherms for a Lennard–Jones fluid confined in a disordered mesoporous material are identical with both methods. Thus the GCMC phase–space sampling

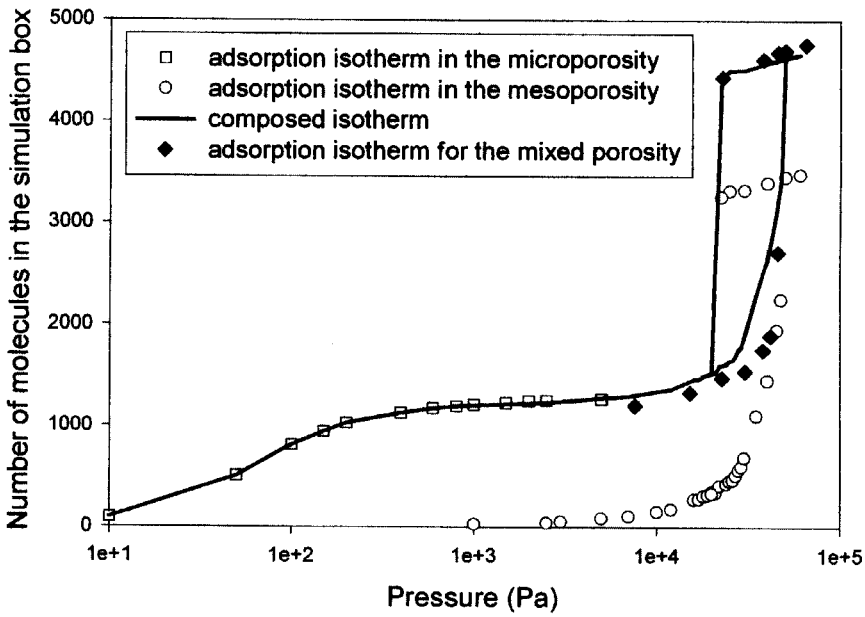

FIGURE 11 Comparison between the composed isotherm and that obtained directly from GCMC calculations of the mixed porosity material.

scheme is not at fault and does nicely describe capillary condensation. However, one may legitimately think that some cautions must be taken because of the standard GCMC algorithm, which allows creation and destruction of particles anywhere in the system bypassing pore constrictions. Indeed, it is known from GCMD results of a Lennard–Jones fluid confined in an ideal model describing a mixed porosity material made of small micropores giving access to a larger pore that freezing (due to the adsorbate/solid interactions) of the adsorbed phase in the microporosity can lead to a pore blocking effect [27]. In our particular case, such effect may not be relevant since access to mesoporosity does not depend on a diffusion step through the microporosity; the mesoporosity in our system being not surrounded by a microporous matrix. In fact the converse is most probable, mesoporosity makes easier the access to microporosity.

CONCLUSIONS

A GCMC study of xenon adsorption in a mixed (micro and meso) porosity silica CPG is presented. A numerical sample of such a CPG adsorbent has been obtained by using an off-lattice reconstruction method recently introduced to reproduce

topological and morphological properties of correlated disordered mesoporous materials: the off-lattice functional of (100 m^2/g)-Vycor is applied to a simulation box containing silicon and oxygen atoms of orthorhombic silicalite. A realistic surface chemistry is obtained by saturating all oxygen dangling bonds in the mesoporosity with hydrogen. The Xe adsorption/desorption isotherms at 195 K shows that the difference of energetics between zeolitic micropores and CPG mesopores lead to two distinct adsorption processes which occur consecutively: (i) micropore filling (ii) adsorption and condensation in the mesopores.

As a consequence, both the microporosity and the mesoporosity can be calculated independently. We suggest that the use of xenon at 195 K may be an efficient way to distinguish between microporous and mesoporous volumes which can be directly evaluated, thanks to a straightforward analysis of the isosteric versus loading curve.

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