Predictions for molecular hydrogen adsorption in microporous carbons via molecular dynamics simulations and a suggestion for a hydrogen storage medium

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Abstract

This work aims at resolving the discrepancy between theoretical predictions on the physical adsorption of molecular hydrogen on carbonaceous solids, by exploiting molecular dynamics simulations of the adsorption process. In continuance of our previous work, three models were constructed for the depiction of the microporous carbonaceous structure. The first one (SSM) consisted of only two parallel sheets, being the lightest one used. The second (IHM) and third (HWM) models comprised structural imperfections in the form of pits and holes into their structure. Structural imperfections seemed to have a slight augmentative effect on the adsorption process. It was concluded that the addition of extra sheets to the walls did not result to any enhancement of the adsorption efficiency of the solid model. On the contrary, the lightest model exhibited superb results for the % weight-by-weight adsorption of hydrogen, approaching the highest value reported. Finally, a couple of suggestions on the development of a material for the storage of hydrogen were derived, based on the above conclusions.
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1. Introduction

The efficient use of hydrogen as a fuel is mainly hampered by the lack of a proper medium for its storage. Storage media have to be cheap, light and in compliance with national and international safety laws. Additionally, hydrogen extraction has to be totally reversible. The search for suitable media for hydrogen storage is obstructed, due to the above requirements. In addition, US DOE has set as a lower limit for storage at 6.5% w/w (extractable hydrogen).

Among the storage methods proposed so far (physical adsorption, chemisorption, liquefaction, compression, metal hydride formation), physical adsorption seems to be the most prominent one. Numerous research groups have investigated adsorption of hydrogen in a large group of solid materials [1–47]. The most popular materials for hydrogen storage are of carbonaceous nature, especially microporous activated carbons, activated carbon fibers (ACF) and carbon nanotubes.

Unfortunately, the results for the adsorption efficiency for all of these materials are controversial.

Carbon nanotubes are a relatively new class of carbonaceous materials. Reported experimental and theoretical results for hydrogen storage in these materials range from 0.3 to 20% w/w [8–40]. Carbon nanotubes' advantage lies in the fact that their structure is virtually known, thus leading to association of experimental data to theoretical predictions. On the other hand, due to their manufacturing process they may contain elements, which affect the adsorption mechanism.

Experimental conditions of the above mentioned studies greatly vary. Several theoretical studies showed that the DOE-proposed limit of 6.5% w/w could not be achieved [30–41]. More recent theoretical works have dealt with the possible insertion of lithium or potassium atoms into the structure of these nanotubes. The intercalation of these atoms led to great increases for the % w/w adsorption of hydrogen in these materials [25–29].

Microporous activated carbons have been long used for the adsorption of gases. Hydrogen adsorption has attracted

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considerable attention during the last 10 years. Unfortunately, both the experimental data and the theoretical predictions are contradictory. The main difficulty in associating experimental and theoretical works is the vast chemical and structural heterogeneity of these materials. Experimental studies [42–45] have provided results for the % w/w adsorption in the range 0.5–5.5% w/w depending on the solid used. In the same way, theoretical studies have provided results ranging from 0.03 to 23.764% w/w for different models used [7,46,47].

Among the most recent studies, Georgakis et al. [7] reported theoretical predictions for the % w/w hydrogen adsorption in microporous carbonaceous solid models and in oxygenated microporous carbonaceous solids, at 77 K. Predictions ranged from 0.67 to 4.41% w/w and 0.21 to 3.30% w/w for the basic and the oxygenated models, respectively, depending on the pore size used. Ye et al. [6] proposed a nanocontainer for the storage of molecular hydrogen, which consisted of a (20.0) SWNT combined with two C_{60} fullerenes in its interior that served as molecular valves. Deploying molecular dynamics calculations they reported maximum hydrogen adsorption of 7.7% w/w at pressures higher than 10,000 bar. Another recent study [5] stated that carbon nanotubes offered no advantage compared to activated carbons for hydrogen storage. In this study, a maximum of 9.2% w/w hydrogen adsorption was reported for adsorption on slit shaped pores, while an optimum adsorption temperature of 115 K was proposed. Lee et al. [4] dealt with the adsorption properties of surface modified ACF for hydrogen storage. Their ACF doping with Ni and F findings showed a continuous increase of hydrogen adsorption although the micropore volume of the ACFs decreased substantially during the doping procedure. Georgiev et al. [2] studied hydrogen adsorption both experimentally and theoretically (DFT) on high purity chemically activated carbon near triple point. An adsorption maximum of 4% w/w was acquired at these conditions, while for room temperature hydrogen adsorption was virtually absent. A pore size of 6.0 Å was reported as the starting point of hydrogen adsorption. Thomas [1] concluded that hydrogen adsorption on porous carbons can reach 5% w/w at 77 K but only 0.5% w/w at ambient temperatures and high pressures.

Evidently, a large gap exists between theoretical predictions and experimental results for the adsorption of hydrogen on microporous carbons. Another gap is illustrated between the theoretical prediction of 23.764% w/w hydrogen uptake [47] and the most of the rest predictions on heavy carbonaceous models and oxygenated carbonaceous models. This paper aims at revealing the reasons for this discrepancy between these studies, using at least one lighter solid model. The effect of structural imperfections of the solid structure on hydrogen adsorption process is also examined. Three new pore models were constructed for this purposes, and used for molecular dynamics simulations of hydrogen adsorption in their micropores.

2. Structural modeling and simulations

In continuance of our previous work, new solid models needed to be constructed. For the creation of these solid
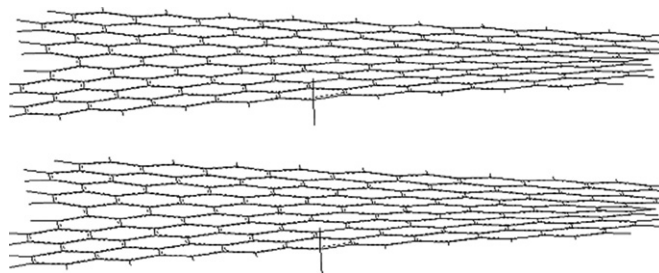

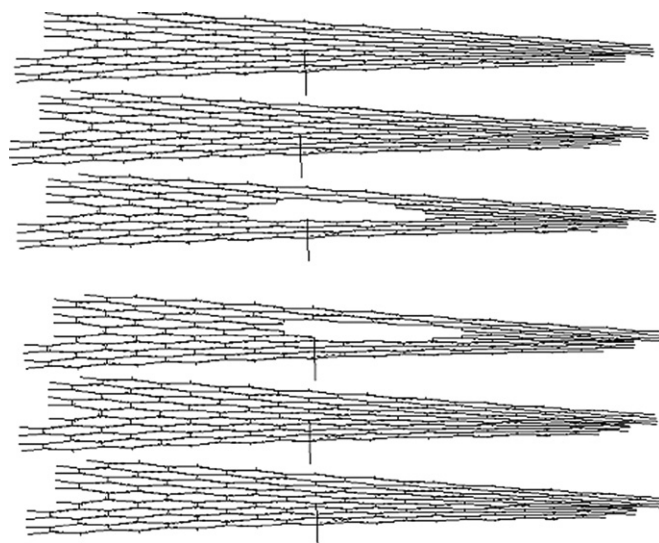
Fig. 1. The single sheet model (SSM).

Fig. 2. The inner holes model (IHM).

models, two model sheets were first developed. The basic structural unit designed, was a planar sheet of dimensions 20×25 Å (approximately). This purely carbonaceous sheet consisted of benzene rings placed side by side. In order to construct the structural imperfections of the solid models, an alteration of the basic sheet was created with the removal of 12 benzene rings from its center, forming a pseudo-hole of approximate diameter of 8.5 Å and a surface area of 51 Å^2. Three solid models were constructed using the two sheets described above.

The single sheet model (SSM, Fig. 1) consists of two parallel carbonaceous sheets. This model was constructed for comparison reasons to the heavier pore models of our previous work that consisted of six parallel carbonaceous sheets.

Putting together four basic sheets and two altered ones at 3.34 Å apart in the way shown in Fig. 2, resulted to the development of the inner hole model (IHM, Fig. 2). IHM accounts for a heavy solid model, with material loss from its interior, possibly due to a chemical reaction in an oxidizing environment (activation). The sheet-to-sheet distance was set at 3.34 Å in order to resemble the structure of graphite, for comparison to our previous results.
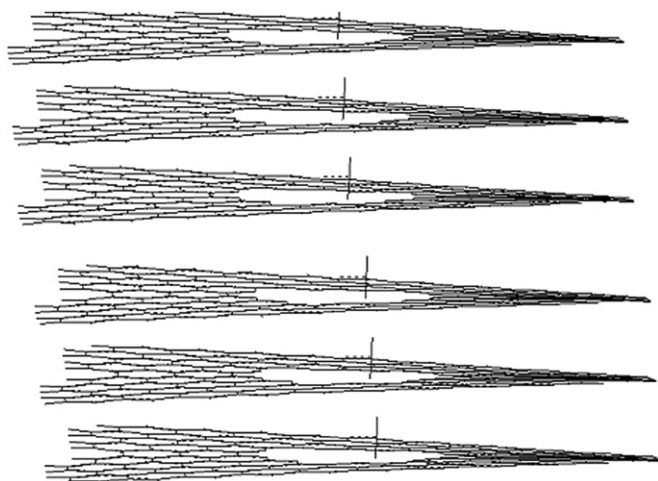
Fig. 3. The hollow walls model (HWM).

Table 1

Model	Weight (a.u.)
Planar carbonaceous sheet	2393.47
Hollow carbonaceous sheet	2237.33
SSM	4786.94
IHM	14048.54
HWM	13423.98
Carbonaceous slit shaped model [7]	14360.82
Oxygenated slit shaped model [7]	16029.30

Putting together six altered sheets as 3.34 Å apart resulted to the development of the hollow walls model (HWM, Fig. 3). HWM accounts for a heavy solid model, with severe material loss from its mass, possibly due to a chemical reaction in an oxidizing environment, which resulted to the formation of a hole throughout its structure. The weights of the basic structures used (planar and hollow sheet), the three models constructed (SSM, IHM, HWM) and the models of our previous study are presented in Table 1.

Due to comparison reasons with our previous results, slit pore diameters in the range 5–20 Å were examined.

Hydrogen was considered to be in molecular form. It was used in "clouds" of 300 hydrogen molecules, which were first allowed to equilibrate at the simulation temperature of 77 K. The latter is the typical temperature of experimental hydrogen adsorption tests.

Hydrogen adsorption on the three model solids described above (SSM, IHM and HWM) was examined by molecular dynamics simulations. The time step was set at 10^{-16}–10^{-15} s and the total simulation time exceeded 450 s per simulation. If longer time steps were used, the system could not reach adsorption equilibrium due to the shorter vibration times of the hydrogen–hydrogen bond. If shorter time steps were used, the simulation time would exceed acceptable limits.

All simulations were performed using multiple licenses of the HyperChem 7.5, HyperCube, USA software. We used four licenses in order to complete our study.
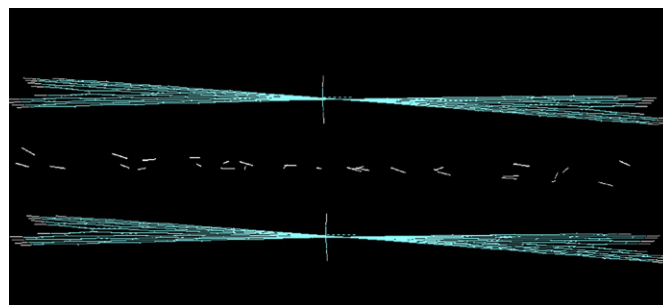

Fig. 4. A snapshot of the adsorption process in the 5.32 Å SSM pore. Adsorbed layer lie parallel to pore walls (simulation time of 290 ps).
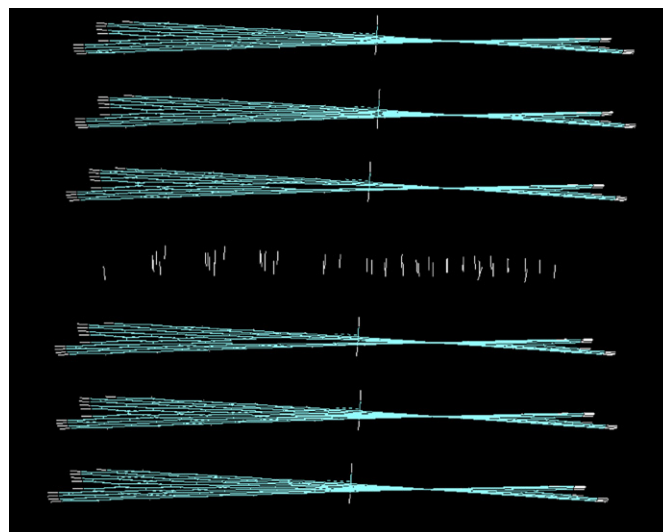

Fig. 5. A snapshot of the adsorption process in the 7 Å IHM pore. Hydrogen molecules lie perpendicular to pore walls, using all available space (simulation time of 340 ps).

3. Results—discussion

The three model structures used in this study are presented in Figs. 1–3. In contrast to our previous work, all carbonaceous planar layers are almost flat. The major distortions in the planarity of our previous work models were caused due to the presence of oxygen functional groups in the second model used. The absence of a number of benzoic rings from the two out of three models designed in the current work does not seem to cause any distortions to their originally graphitic planarity.

Snapshots of the adsorption process in the three models were acquired at various simulation times. Such snapshots are presented in Figs. 4–6 for all models used at different simulation times. Cautious observation of these snapshots reveals that the adsorption mechanism seems to be similar for all slit shaped models, contrary to the situation confronted in our previous work. The presence of the pits in the IHM exhibits no alteration of the hydrogen molecules configuration inside the slit shaped pore. In the case of the HWM the situation is slightly different, as the holes permit the entrance of a total of 18 hydrogen molecules (three molecules per sheet). Considering the
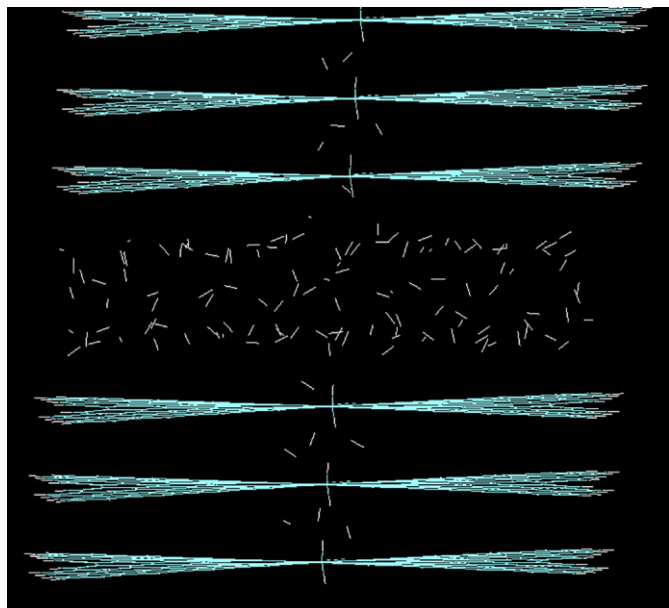
Fig. 6. A snapshot of the adsorption process in the 10 Å HWM pore. Hydrogen molecules have not reached adsorption equilibrium yet (simulation time of 440 ps).

Table 2
Pore sizes for hydrogen adsorption initiation in the three solid models used

Solid model	Pore size (Å)
SSM	5.32
IHM	5.30
HWM	5.29

diameter of the pseudo-cylindrical holes (approximately 8.5 Å in diameter) and the results of our previous work [7], it is expected that the widening of the holes (up to 10–11 Å in diameter) would favor the creation of an additional layer inside the hole of each sheet, thus increasing the adsorption efficiency of the holes.

Molecular dynamics simulations showed that adsorption starts at a critical pore width ranging from 5.29 to 5.32 Å, as indicated in Table 2. The differences between the adsorption starting points for the three pore models are extremely small and they are expected neither to control the adsorption process nor to be useful in the design of storage media for hydrogen. Nevertheless, such small differences may be attributed to calculation errors.

Examination of Figs. 4–6 shows that the first adsorbed layer of hydrogen molecules in all models is formed parallel to the slit pore walls. The parallel alignment allows for the entry of hydrogen molecules in narrower pores as has already been established in our previous work. As the pore width increases, the alignment of the first adsorbed layer transforms to vertical. Adsorption progresses with the formation of initially parallel-aligned layers, which rapidly turn to vertically aligned layers.

In agreement with our previous work, critical pore sizes were identified, in which consecutive layer formation took place. The critical sizes are of great importance for the design of materials for hydrogen storage, as has already been discussed [7]. The appearance of optimum pore widths has also been reported by others [2]. These critical sizes (Table 3) are comparable but not exactly equal for the three pore models used. This inequality indicates a small variation in the adsorption field caused by the structural differences (number of layers, number and depth of the holes) of the three models. The adsorption effectiveness of the three models is virtually equal, as can be established from Table 3. The three pore models accomplish the formation of seven parallel layers (for the widest pores used), proving their comparable adsorption field capability. The greatest difference between the critical sizes of the three models is 1.3 Å, while the distance between two consecutive critical sizes (for a given pore model) ranges from 1.90 to 3.65 Å, depending on the number of layers already formed inside the model pores (Table 3).

Layer formation causes variations in the adsorption density of hydrogen inside the three model solids. Adsorption density is higher than the liquid hydrogen density ($0.071\,\text{g cm}^{-3}$) for the three models (Table 4) and for sizes greater than 7.5 Å, as

Table 3
The critical pore sizes for the consecutive layer formation for the three models used

Layer no.	1	2	3	4	5	6	7
Critical pore sizes for the SSM (Å)	5.32	7.75	10.1	12.25	14.80	16.95	19.00
Critical pore sizes for the IHM (Å)	5.30	7.65	9.90	13.55	15.90	17.95	19.90
Critical pore sizes for the HWM (Å)	5.29	7.85	10.2	13.25	15.15	17.20	19.10

Table 4
Adsorption density and % w/w adsorption for the three models used in this study

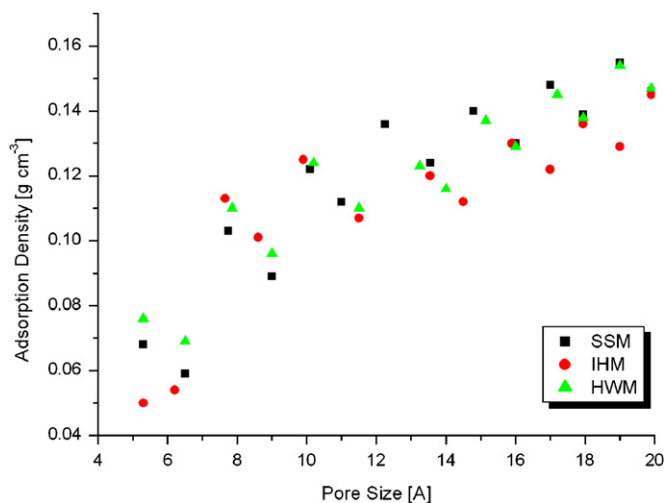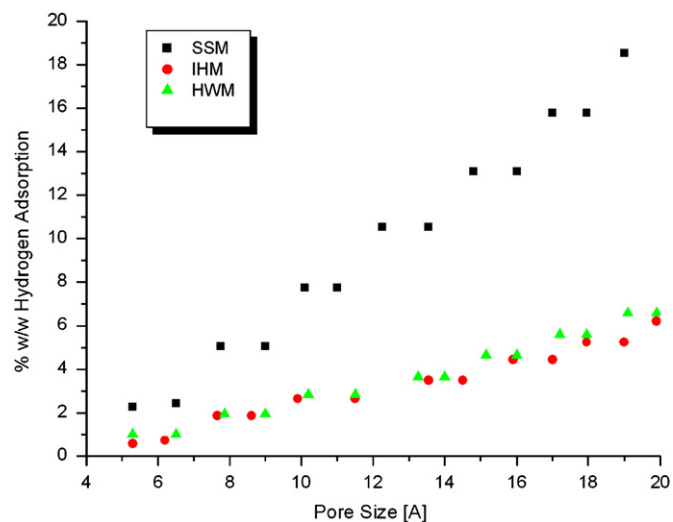| Pore size (Å)/solid model	5.29	5.30	5.32	7.00	10.00	15.00	20.00
% w/w adsorption—SSM	—	—	2.27	2.61	5.26	12.93	18.53
% w/w adsorption—IHM	—	0.57	0.57	0.93	2.15	3.62	6.33
% w/w adsorption—HWM	1.01	1.01	1.01	1.1	2.25	3.90	6.91
Adsorption density (g cm^{-3})—SSM	—	—	0.068	0.059	0.083	0.137	0.147
Adsorption density (g cm^{-3})—IHM model	—	0.05	0.05	0.060	0.099	0.111	0.146
Adsorption density (g cm^{-3})—HWM	0.076	0.076	0.076	0.064	0.096	0.113	0.151

Fig. 7. Hydrogen adsorption density.

Fig. 8. Hydrogen % weight-by-weight adsorption.

has been also reported in our previous work and by others as well [48–54]. In compliance with the similarity of the number of layers formed in each pore model, hydrogen density in also comparable for the three pore models. Adsorption density ranged from 0.05 to 0.151 g cm^{-3} for the pore sizes 5–20 Å. The three pore models exhibited comparable minima and maxima of adsorption densities, as can be seen in Fig. 7. Adsorption density follows a sigmoid pattern exhibiting local maxima, gradual decreases, local minima, stiff increases ("jumps") and local maxima again. This behavior has already been explained by the appearance of critical sizes at which multiple layer formation takes place. Adsorption density peeks at these critical points (with sudden "jumps") and diminishes gradually between them, causing this sigmoid behavior.

Hydrogen amount adsorbed % w/w is presented in Table 4. In contrast to adsorption density behavior, % weight-by-weight hydrogen adsorption exhibits a step increase between the critical sizes, as can be seen in Fig. 8. The difference between the two patterns is that adsorption density depends on the pore size, whereas % weight-by-weight adsorption does not, as already discussed.

The IHM and HWM exhibit comparable results for the whole range of pore sizes used (5–20 Å). Specifically, IHM exhibits hydrogen adsorption in the range 0.57–6.33% w/w while the HWM exhibits hydrogen adsorption in the range 1.01–6.91% w/w. The differences between them can be almost totally attributed to their weight difference, due to subtraction of more benzoic rings in the HWM. On the other hand, the SSM demonstrates superb results for the % weight-by-weight adsorption, which ranges from 2.27 to 18.53% w/w. The latest result is the second highest reported for carbonaceous materials, being second only to 23.764%, which was reported [47] as the "thermodynamic limit" of the physical adsorption process. Adsorption amount in the SSM surpasses the DOE limit of 6.5% w/w of extractable hydrogen for every pore size greater than 10.5 Å. Similarly, the adsorption amount for the HWM is

higher than the DOE proposed limit for every pore size greater than 19 Å, while for the IHM the respective size is estimated to be at 20.4 Å.

This surprisingly high performance of the SSM can be verified considering the equality of the three models' adsorption efficiencies, as discussed above. Total number of sheets per pore wall seems to play a tiny part in the adsorption field of each pore model. Comparison of adsorption densities and total number of formed layers has already proved that claim. The great difference between the SSM and the other two models is their weight. SSM weights almost less than 33% of the other two models and demonstrates just less than triple amount of % weight-by-weight adsorption. Calculations on the adsorption amounts and the weight of the three models show that the IHM field is only 0.2% more efficient (per mass unit) than the SSM's field, while the HWM is 4.4% more efficient.

Basic principles for the design of a model carbonaceous solid for the storage of hydrogen can be drawn from our results. Our conclusion on the equality of the adsorption fields should be given the appropriate attention. It was shown that the increase of the adsorption efficiency of the pore models was only slightly increased by the addition of extra carbonaceous sheets to the pore walls. Early theoretical approaches had estimated this increase to be as high as 20%, but in this work it was only found to be 0.2% (for the addition of two extra sheets per wall).

Design of a proper material for the storage of hydrogen should aim at the manufacture of a light material, based on the slit shaped pore model. If possible, a combination of SSM and HWM should be pursued. SSM has proved the adsorption efficiency of the light model while HWM has indicated the possible augmentative effect of the carbonaceous sheets' holes. This material's final adsorption efficiency will inescapably rely on its actual size. Great sizes will unavoidably lead to competitive phenomena, which will cause significant decrease of individual pore adsorption efficiency. Thus, the smallest possible sizes of such a material should be used.

4. Conclusions

Continuing our previous work, three new slit shaped carbonaceous pore models (SSM, IHM and HWM) were constructed for the investigation of molecular hydrogen adsorption. SSM comprised two parallel sheets, being the lightest model used. SSM was constructed for comparison reasons to the heavier pore models of our previous work. IHM is a slit shaped model in which every wall comprises three carbonaceous sheets at 3.34 Å apart. From the inner two sheets 12 benzene rings had been removed, forming a hole on the surface with an area of approximately 51 Å^2. HWM's walls also comprise three parallel carbonaceous layers from which 12 benzene rings have been removed, forming a hole in the whole solid structure.

For all three models examined, hydrogen density was found to be higher than the respective liquid hydrogen's density. Multilayer adsorption at critical pore sizes led to a sigmoid behavior of both adsorption density and hydrogen % w/w adsorption.

SSM exhibited outstanding results for the % w/w hydrogen adsorption, reaching as high as 18.53% w/w for the 20 Å pore size. To the best of our knowledge, this result is the second highest reported. On the other hand, IHM and HWM exhibited lower results, ranging from 0.57 to 6.33% w/w and 1.01 to 6.91% w/w, respectively.

Adsorption field equality was proved for the three models, leading to an introductory suggestion for the development of a material for the storage of hydrogen, via physical adsorption. Material's advanced properties will be the subject of a forthcoming work.

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