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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.

Keywords: Molecular hydrogen; Adsorption; Carbonaceous solids; Molecular dynamics; Simulation; Hydrogen storage

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 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.

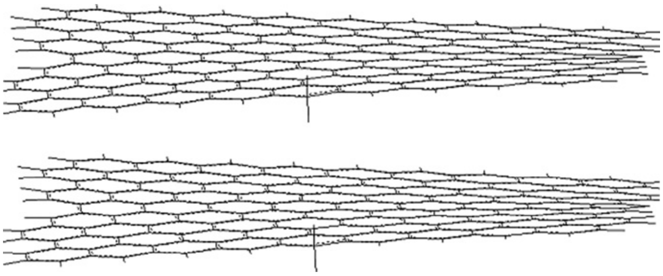

Fig. 1. The single sheet model (SSM).

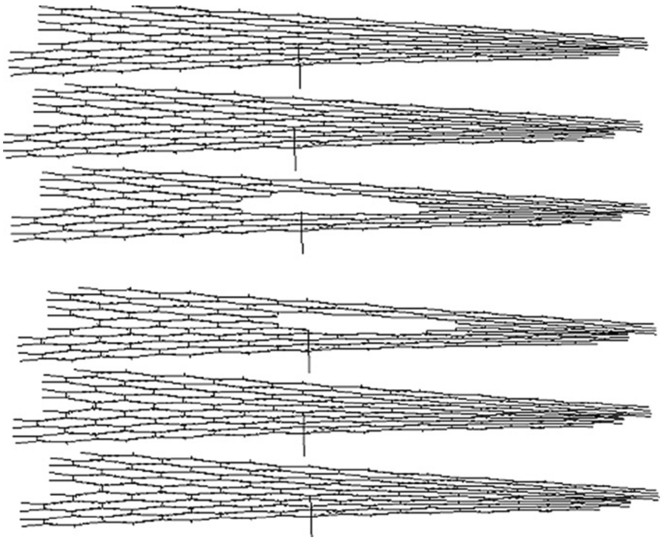

Fig. 2. The inner holes model (IHM).

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.