

Molecular Hydrogen Storage in Fullerenes for Use on Board Fuel Cell Vehicles

D. J. Durbin^{†§}, N. L. Allan[§], C. Malardier-Jugroot[†]

[†]Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario K7K 7B4, Cecile.Malardier-Jugroot@rmc.ca

[§]School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom, N.L.Allan@bristol.ac.uk

ABSTRACT

Hydrogen gas is a promising potential replacement for fossil fuels on board vehicles. However, it cannot be commercially used until an energetically inexpensive method is found which reduces a reasonable mass of H₂ to sufficiently small volume. Carbon nanomaterials are a strong potential candidate for this storage material because they are cheap, lightweight and abundant and can store H₂ through physisorption interactions, which in principle allow H₂ to be removed from the storage material easily. Unfortunately, C–H₂ physisorption interactions are weak and so must be optimized (is optimized the right word here – the conclusion is that physisorption itself is too weak – hence the heme dopants for example which I would call hindered chemisorption) before the storage method becomes viable. Therefore, the current project analysed carbon fullerenes to understand the factors which govern the interactions and so indicate the most favourable systems for further study.

Keywords: hydrogen storage, carbon nanomaterials, fullerenes, curvature, physisorption, fuel cell vehicles

1 INTRODUCTION

Hydrogen gas is a strong candidate to replace gasoline in automobiles because, at 143.0 MJ/kg, it has the highest energy density of common fuels by weight (ca. three times larger than gasoline). Unfortunately, storage is difficult because, at 0.0108 MJ/L, gaseous H₂ also has the lowest energy density by volume (over 3000 times smaller than gasoline) and it is highly diffuse and buoyant.¹ Thus hydrogen cannot be used as a fuel until compact and efficient storage techniques are developed. Traditional mechanical storage methods of compression and liquefaction are energetically and financially expensive. In addition, neither technique compresses H₂ to a sufficiently small volume.²⁻⁴

Alternative storage methods are currently under development. These include metal and non-metal hydrides and absorption on carbon substrates. None of these techniques are presently viable because they have unacceptably low gravimetric or volumetric densities; many systems also require high pressures and low temperatures.⁵⁻

¹⁰ Due to the failure of these techniques, hydrogen

adsorption on carbon nanomaterials has become an increasingly prominent field over the last few decades. Carbon structures are a potential cheap, abundant and light weight storage system.¹¹⁻¹⁵

There are two main approaches to hydrogen storage on large area carbon nanomaterials. The first, hydrogen chemisorption, is impractical because both the adsorption and desorption of hydrogen have energetic barriers in the order of electron volts.¹⁶ The other method is via physisorption. This in principle utilizes the advantages of carbon nanomaterials without introducing potentially problematic chemical reactions. Unfortunately, dispersion forces between carbon and hydrogen are weak. As a result, carbon substrates are often activated by introducing areas of sp³-hybridized carbon or decorating with alkali or transition metals.¹⁷⁻¹⁹ These modifications allow the substrate to contribute more electron density to the C–H₂ interaction and so increase the material's storage capacity. However, even with these enhancements, low temperatures and high pressures are required to achieve acceptably high hydrogen storage capacities.

Recent analysis suggests that hydrogen storage in CNTs is more promising than in planar carbon substrates because H₂ physisorption is more favourable on curved surfaces where the surface strain provides more potential for C–H₂ interactions.²⁰⁻²¹ Properties such as carbon bonding sites, orientation of H₂ and substrate curvature have been considered. However, most analyses were performed using only a few carbon atoms, sometimes as little as five.²¹⁻²⁵ Therefore, these studies did not allow for the effects of multiple carbon interactions with one H₂ molecule, which can occur in large systems. Consideration of only a small surface section can also be liable to spurious edge effects.

To avoid such problems, the present study uses DFT to model H₂ interactions with full C_{*n*} (*n* = 20, 60, 180, 540, 960) systems and compares them to single-walled carbon nanotubes (SWCNTs) and graphene. Adsorbed and substitutional platinum and boron, nitrogen and oxygen substitutional dopants are considered in an attempt to increase the C–H₂ physisorption interaction. Hydrogen does not form a chemical bond with platinum due to steric hindrance when H₂ is located inside the fullerene. This work extends previous studies by the authors, which have shown that modification of a graphene/Pt substrate can have a large effect on the interaction of the substrate with small gas molecules. This was observed when the presence of N,

B or O substitutional dopants in a graphene/Pt layer notably reduced the substrate's interaction with H₂.²⁶⁻²⁷

2 METHODS

All simulations were performed using DFT as implemented in the *Gaussian 09* software package.²⁸ The B3LYP functional and LANL2MB basis set were used to perform an initial analysis of H₂ interactions in all systems. An empirical dispersion correction was then added using the DFT-D3 program.²⁹⁻³⁰

More detailed analyses were performed on the most interesting systems with the more computationally expensive B97D functional. B97D includes dispersion interactions, which are very important when analyzing the relationship between H₂ and carbon. Two basis sets were used for these calculations.

Calculations were carried out for complete fullerenes containing up to six internal H₂ molecules, one adsorbed or substitutional Pt atom and one to three substitutional non-metal dopant atoms where applicable. One non-metal dopant was included in systems that also contained Pt; three were used in systems without Pt, arranged in an alternating pattern within one benzene ring. Similar systems containing a large carbon surface with a limited number of dopant atoms have been shown to be effective in previous studies by the authors.^{36,37}

SWCNTs of the form (*m,m*) where *m* = 3, 5, 9 were modeled in a similar fashion. These nanotubes were chosen because they have similar diameters to C₂₀, C₆₀ and C₁₈₀ respectively and so are most useful for analyzing confinement effects. An 8.5Å segment of nanotube was considered. Periodic boundary conditions were applied to the segment when the less computationally expensive B3LYP functional was used; the nanotube was hydrogen terminated when the B97D functional was applied. Graphene sheets were modeled with a hydrogen-terminated 14.5 × 14.8 Å section for both functionals.

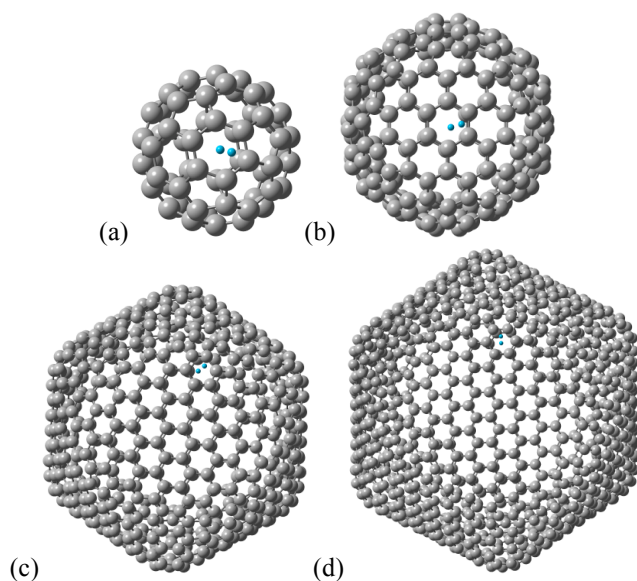


Figure 1: Geometry of C₆₀ (a), C₁₈₀ (b), C₅₄₀ (c) and C₉₆₀ (d) containing internal H₂.

Coordinates for the structures of the smaller fullerenes ($20 \leq n \leq 540$) were obtained from the *Computational Chemistry List, Ltd.* on-line fullerene database compiled by Cramer at the University of Minnesota. Coordinates for the C₉₆₀ structure were provided by Henrard at the University of Namur. Coordinates for the SWCNTs were generated by TubeGen On-line (version 3.4) created by Frey and Doren at the University of Delaware. All systems were optimized without constraints.

Once the structures were optimised, the C–H₂ and H₂–H₂ bond distances and the fullerene–H₂ interaction energy, ΔE (equation 1), were analysed.

$$\Delta E = E_{\text{fullerene:nH}_2} - \left[E_{\text{fullerene:(n-1)H}_2} + E_{\text{H}_2} \right] \quad (1)$$

3 RESULTS AND DISCUSSION

3.1 Effects of Fullerene Diameter

Analysis of C_{*n*} fullerenes with increasing diameters (*n* = 20, 60, 180, 540, 960) found that there is a notable correlation between fullerene size and C–H₂ interaction energy (Fig. 1). Dihydrogen C₂₀ has a large repulsive interaction of 509 kJ/mol. In contrast, H₂ in C₆₀ has a favourable interaction of -27 kJ/mol. In the larger C₁₈₀ fullerene, this decreases to -4 kJ/mol. In the largest C₅₄₀ and C₉₆₀ fullerenes, the C–H₂ interaction becomes negligible, similar to that observed on graphene.

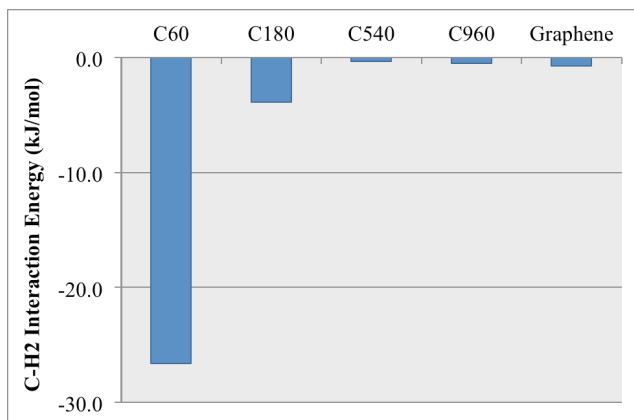


Figure 2: C–H₂ interaction energy (kJ/mol) of one H₂ molecule in C₆₀, C₁₈₀, C₅₄₀, C₉₆₀ and graphene calculated with B3LYP and LANL2MB.

There are several factors likely to contribute to the smaller magnitude of the C–H₂ interaction energy between C₆₀ and C₉₆₀. One factor is the decreasing curvature of the fullerenes as size increases. The four analysed fullerenes are shown in Figure 2. It is observed that the compound shape changes from spherical (C₆₀) to polyhedral (C₉₆₀). And the C–H₂ interaction in the larger fullerenes is similar to that of flat graphene.

This study also found that the shortest C–H₂ distance present in a fullerene/H₂ system influences the magnitude and favourability of the C–H₂ interaction. An optimum C–H₂ distance was observed in C₆₀, C₁₈₀, C₅₄₀ and C₉₆₀ at ca. 2.9 Å, the combined van der Waals radii of carbon and hydrogen. However, when H₂ is forced into the smaller C₂₀ fullerene, where a minimum distance of 2.9 Å cannot be achieved, repulsive interactions dominate.

3.2 Effects of Multiple H₂ Molecules

Favourable interactions are observed for H₂ in C₆₀, C₁₈₀, C₅₄₀ and C₉₆₀ when only one dihydrogen molecule is present. The C–H₂ interactions often become unfavourable, however, when more H₂ is placed in the fullerene. Addition of a second H₂ molecule to C₆₀ requires an energy input. In contrast, six H₂ molecules can be added to C₁₈₀ without unfavourable C–H₂ interactions. The small size of C₆₀ forces the C–H₂ distance below 2.9 Å upon the addition of multiple H₂ molecules. On the contrary, even with six dihydrogens in C₁₈₀ the C–H₂ distance does not decrease below 2.9 Å.

3.3 Effects of Dopants

Both platinum and boron, nitrogen or oxygen dopants were found to have a minimal effect on the C–H₂ interaction. Exohedral Pt does not affect internal H₂ because it is located on the opposite side of the fullerene surface and the potential for Pt–H₂ chemisorption is not sufficient to cause deformation of the fullerene.

Substitutional Pt does not have the same physical barrier of carbon atoms separating it from the H₂ molecule. However, the electron density of substituted Pt is involved in Pt–C interactions and so is unavailable for Pt–H₂ interactions. As a result, the C–H₂ interactions are not affected by any form of adsorbed platinum.

Boron, nitrogen or oxygen substitutional dopants were also investigated in undecorated fullerenes and those containing Pt. Previous projects by the authors found that addition of a non-metal dopant to a graphene surface affected the binding of platinum to the surface, which in turn affected chemisorption between Pt and H₂.³⁷ However, the same effect was not observed for the physisorption interactions investigated in the present study. Similarly, 5% substitution by like heteroatoms (three heteroatoms in C₆₀) had a negligible effect on H₂ physisorption.

3.4 Effects of Confinement

To further understand H₂ storage in curved carbon nanomaterials, the effects of 2-dimensional versus 3-dimensional confinement were studied by comparing fullerenes (3D confinement) with (*m,m*) SWCNTs (2D confinement) of similar diameters. C₂₀, C₆₀ and C₁₈₀ fullerenes were contrasted with (3,3), (5,5) and (9,9) SWCNTs respectively.

As is shown in Figure 3, identical trends in C–H₂ interaction energy are found for the 2D and 3D systems. However, a difference is observed in the magnitude of the interaction energies. In all cases, there is a stronger interaction when confining H₂ in a 3D structure; there is a larger number of C–H₂ interactions in the 3-dimensionally confined system. Each C–H₂ interaction contributes to the total observed interaction energy.

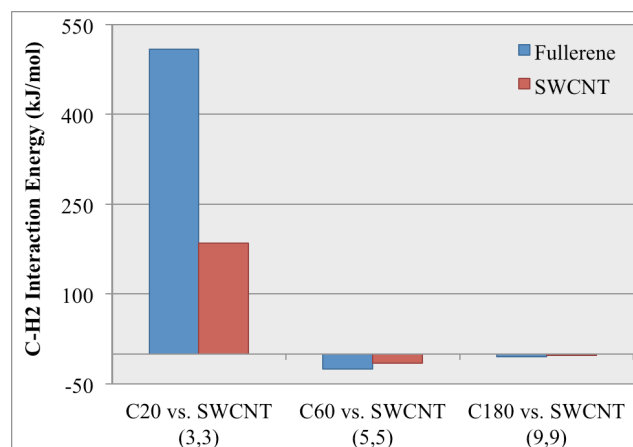


Figure 3: The C–H₂ interaction energy (kJ/mol) of one H₂ molecule in C₂₀, C₆₀ and C₁₈₀ compared with SWCNTs of similar diameter ((3,3), (5,5) and (9,9) respectively) calculated with B97D and 6-311G(d,p).

4 CONCLUSIONS

Hydrogen gas is a promising potential replacement for fuel cells on board vehicles. However, its use is currently limited by insufficient storage methods. Carbon nanomaterials are a prospective storage material, but they must first be optimized to encourage sufficiently favourable C–H₂ physisorption interactions. The present study finds that carbon nanomaterials can be optimized by synthesizing a geometry that encourages a C–H₂ distance near 2.9 Å and allows for the maximum number of C–H₂ interactions. This can be accomplished by storing H₂ inside a curved carbon nanomaterial. Platinum and boron, nitrogen or oxygen dopants were not found to increase C–H₂ interactions. However, early work modifying the structures in order to hinder chemisorption sterically appears to be promising and is currently under investigation by the authors. Non-carbon nanomaterials, such as those made from silicon, are also under investigation.

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