A First Principle Comparative Study on Chemisorption of H₂ on C₆₀, C₈₀, and Sc₃N@C₈₀ in Gas Phase and Chemisorption of H₂ on Solid Phase C₆₀

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The chemisorptions of H₂ on fullerenes C₆₀ and C₈₀, endofullerene Sc₃C₆₀ and solid C₆₀ were comparatively studied. A chain reaction mechanism for dissociative adsorption of H₂ on solid C₆₀ is proposed under high pressure. The breaking of H–H bond is concerted with the formation of two C–H bonds on two adjacent C₆₀ in solid phase. The adsorption process is facilitated by the application of high pressure. The initial H₂ adsorption on two adjacent C₆₀ gives a much lower barrier 1.36 eV in comparison with the barrier of adsorption on a single C₆₀ (about 3.0 eV). As the stereo conjugate aromaticity of C₆₀ is destructed by the initial adsorption, some active sites are created. Hence the successive adsorption becomes easier with much low barriers (0.6 eV). In addition, further adsorption can create new active sites for the next adsorption. Thus, a chain reaction path is formed with the initial adsorption dominating the whole adsorption process.

1. Introduction

From the beginning of the “fullerene area,” hydrogenated fullerenes have attracted wide-spread attention due to their potential application. It may not only be interesting for hydrogen storage [1–5], but also be used as an additive for lithium ion cells to significantly prolong the lifetime of these cells [6]. Experimentally, studies on the interaction between hydrogen and fullerenes have been focused on the chemical process of hydrogenation, with the products C₆₀Hₓ and C₇₀Hₓ being of fundamental interest as a model for other fullerene derivatives [7, 8]. A variety of chemical procedures have been devised to produce hydrogen radicals that could adsorb readily on these carbon atoms, using either reducing reagents [1, 9, 10], or catalysts [11]. In addition, direct hydrogenation of C₆₀ and C₇₀ has also been achieved without the usage of a catalyst by exposing solid-phase fullerenes to high-pressure hydrogen gas (0.5–30 kbar) at elevated temperature (500–600 K) [4].

Theoretically, hydrogen storage based on fullerene materials has attracted many attentions. Using first principle calculations based on density functional theory, Sun and coworkers reported that each B₃₆C₃₆ cage can store at most 18 hydrogen molecules at zero temperature [12]. They also find that an isolated Li₁₂C₆₀ cage where Li atoms are capped onto the pentagonal faces of the fullerene not only is very stable but also can store up to 120 hydrogen atoms in molecular form with a binding energy of 0.075 eV/H₂ [13]. Zhao and coworkers report that a particular Scandium organometallic buckyballs can bind as many as 11 hydrogen atoms per transition metal, which gives the maximum retrievable H₂ storage density 9 wt% [14]. Kang and coworkers reports that Ni-dispersed fullerenes are considered to be capable of...
storing 6.8 wt% H₂, with H₂ desorption activation barrier of 11.8 kcal/mol, which is ideal for many practical hydrogen storage [15].

However, the mechanism for direct reactions between H₂ and these fullerenes remains unexplained to the best of our knowledge. Chan et al. proposed the mechanism of H₂ molecule dissociative chemisorption on the close cousin of fullerences, carbon nanotubes, in solid phase under high pressure [16]. The breaking of the H–H bond is concerted with the formation of two C–H bonds on two adjacent carbon nanotubes in solid phase, facilitated by the application of high pressure which shortens the interstitial distance between nanotubes. The adsorption behavior gives some hints on H₂ adsorption on fullerences.

In this work, we proposed a chain reaction mechanism for H₂ molecules dissociative adsorption on solid C₆₀ under high pressure. In comparison, we also studied H₂ adsorption on the most stable fullerences C₆₀ and C₈₀ in gas phase as well as endofullerenes Sc₃N@C₈₀.

### 2. Computational Method

The first principles total energy and electronic structure calculations were carried out within the framework of DFT [17] with a plane wave basis set and pseudopotentials for the atomic cores, as implemented in the Vienna ab initio simulation package (VASP) [18, 19]. The PW91 gradient correction was added to the local density exchange-correlation functional and projector augmented wave (PAW) pseudopotentials [20, 21] were employed, with an energy cutoff of 400 eV for the plane-wave expansion as these approaches have successfully applied to similar systems [16]. The supercell is sampled with a 1 × 1 × 1 k-point mesh, generated by the Monkhorst-Pack algorithm. The convergence criteria were 1.0 × 10⁻⁵ eV for the SCF energy, 1 × 10⁻⁵ eV for total energy, and 0.05 eV/Å for atomic force, respectively.

A climbing image nudged elastic band method was used to locate the transition states [22–24]. The vibrational frequencies and normal modes were calculated by diagonalization of the mass-weighted force constant matrix, which was obtained using the method of finite differences of forces as implemented in VASP. The ions are displaced in the +/− directions of each Cartesian coordinate by 0.02 Å. There is only one imaginary frequency for all these structures, indicating that they are indeed the transition states in the potential energy surface.

The adsorption energies (E_ads) for the adsorption of H₂ on fullerences were calculated by

\[
E_{\text{ads}} = E(\text{fullerene} + \text{H}_2) - \left[ E(\text{fullerene}) + E(\text{H}_2) \right],
\]

where \(E(\text{fullerene} + \text{H}_2), E(\text{fullerene})\), and \(E(\text{H}_2)\) are the total energies of H₂ adsorbed fullerene, total energies of fullerene (fullerene = C₆₀, C₈₀, Sc₃N@C₈₀), and the total energies of H₂, respectively. The larger adsorption energy indicates the stronger adsorption.

### Table 1: Energy barriers and reaction energies (ΔE) for H₂ adsorption on C₆₀, C₈₀ and Sc₃N@C₈₀ in gas phase. Energies are given in eV.

<table>
<thead>
<tr>
<th>Absorption site</th>
<th>Barrier (eV)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆₀</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-6 parallel</td>
<td>3.68</td>
<td>−0.87</td>
</tr>
<tr>
<td>6-6 perpendicular</td>
<td>3.57</td>
<td>−0.86</td>
</tr>
<tr>
<td>5-6 parallel</td>
<td>3.04</td>
<td>−0.10</td>
</tr>
<tr>
<td>5-6 perpendicular</td>
<td>3.05</td>
<td>−0.09</td>
</tr>
<tr>
<td>C₈₀</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-6 parallel</td>
<td>2.47</td>
<td>−0.50</td>
</tr>
<tr>
<td>6-6 perpendicular</td>
<td>2.47</td>
<td>−0.50</td>
</tr>
<tr>
<td>5-6 parallel</td>
<td>2.26</td>
<td>−1.10</td>
</tr>
<tr>
<td>5-6 perpendicular</td>
<td>2.27</td>
<td>−1.10</td>
</tr>
<tr>
<td>Sc₃N@C₈₀</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc non-bonded C</td>
<td>3.60</td>
<td>−0.14</td>
</tr>
<tr>
<td>Sc bonded C</td>
<td>3.78</td>
<td>−0.04</td>
</tr>
</tbody>
</table>

### 3. Results and Discussion

#### 3.1. H₂ Adsorption in Gas Phase

We firstly consider the H₂ adsorption on fullerenes C₆₀ and C₈₀ and endofullerenes Sc₃N@C₈₀ to explore the possible adsorption media without any catalyst in gas phase. In the calculations, the interactions between H₂ molecule and fullerenes (or endofullerenes) were modeled in a supercell of size 16.0 Å × 16.0 Å × 16.0 Å, with one k-point (gamma point). The energy barriers and reaction energies are listed in Table 1.

3.1. H₂ Adsorption on C₆₀ in Gas Phase. The icosahedral C₆₀ consists of 12 pentagons and 20 hexagons. Hence the bonds can be categorized as two types, pentagon-hexagon bonds (5-6 bond) and hexagon-hexagon bonds (6-6 bond). Addition on adjacent sites such as 5-6 bond and 6-6 bond engenders isomers. Furthermore, addition can take place on nonadjacent sites, which would produce many isomers. For C₆₀H₂, the simplest fullerene dihydride, there are 23 isomers. However, there is only one isomer that has been characterized. Among all kinds of C₆₀H₂ isomers, (1,2) addition products are considered as the most stable. To compare the adsorption difference, we investigated H₂ adsorption on both 5-6 and 6-6 bonds. In addition, two adsorption modes are considered. One case is that the H–H bond of incoming H₂ is to be considered to parallel the 6-6 bond (Structure A and Structure E in Figure 1). The other one is that the incoming H–H bond is to be considered to point perpendicularly to the C–C bond (Structure C and Structure G in Figure 1). Energetically, the total exothermic energy for the formation of the two C–H bonds in 6-6 bond addition production is 0.77 eV favorable than that for 5-6 bond addition (Table 1), indicating that 6-6 bond addition gives the most stable structure. The two adsorption modes result in two possible adsorption mechanisms. The parallel adsorption mode gives a concerted mechanism, in which two H atoms bonded to two C atoms (TS 1 in Figure 1), respectively. In contrast, the perpendicular adsorption mode gives a step mechanism (one H atom is adsorbed first, then the second one, TS 2 in Figure 1). The barriers for both concerted mechanism and step mechanism are so high that the reaction is very difficult.
to take place, although the barrier for the step mechanism is 0.11 eV favorable than that for the concerted mechanism.

3.1.2. H\textsubscript{2} Adsorption on C\textsubscript{80} in Gas Phase. C\textsubscript{80} has the same I\textsubscript{h} symmetry as C\textsubscript{60}, so it can also be served as adsorption media, although experimentally no hydrite of C\textsubscript{80} has been characterized. We carried out the same calculations as we did on C\textsubscript{60} as shown in Figure 2. The 6-6 parallel and perpendicular adsorption modes have the same energy barrier of 2.47 eV whereas 5-6 parallel and perpendicular adsorption
Figure 3: Optimized structures and transition states structures for H\(_2\) molecule adsorption on Sc\(_3\)N@C\(_{80}\) in gas phase. Selective distances are given in Å.

Figure 4: Optimized structures and transition state (TS) structures for the first H\(_2\) dissociative chemisorption on solid C\(_{60}\) array. Selective distances are given in Å.

modes have the same barrier of 2.27 eV. Comparing to that of C\(_{60}\), the calculated energy barrier is about 1 eV lower than that for C\(_{60}\) due to the less stability of C\(_{60}\).

3.1.3. H\(_2\) Adsorption on Sc\(_3\)N@C\(_{80}\) in Gas Phase. As one of the most stable endofullerene, Sc\(_3\)N@C\(_{80}\) has become accessible in macroscopic quantities. Since the adsorption barrier for C\(_{60}\) has decreased more obviously than that for C\(_{60}\), its stable derivative Sc\(_3\)N@C\(_{80}\) is expected to be a promising hydrogenation material. As shown in Figure 3, we considered two different adsorption modes: either adsorption to Sc bonded C or Sc nonbonded C. However, whichever atom H bonds, the calculated energy barriers are more
Table 2: Reaction barriers and reaction energies (ΔE) for the second H₂ absorption on solid C₆₀ with three different absorption modes.

<table>
<thead>
<tr>
<th>Absorption site</th>
<th>Barrier (eV)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,2)-(1,2)</td>
<td>0.76</td>
<td>-2.05</td>
</tr>
<tr>
<td>(1,2)-(1,4)</td>
<td>0.59</td>
<td>-1.82</td>
</tr>
<tr>
<td>(1,4)-(1,4)</td>
<td>0.52</td>
<td>-1.81</td>
</tr>
<tr>
<td>Former absorption</td>
<td>1.21</td>
<td>-1.77</td>
</tr>
</tbody>
</table>

3.2. H₂ Adsorption in Solid Phase. In contrast, the solid phase, composed of bundles of C₆₀, provides a unique chemical environment dependent on the external pressure and makes it much easier for H₂ dissociative chemisorption on C₆₀ bucky balls. In our calculations, the interactions between hydrogen molecule H₂ and C₆₀ were modeled in a supercell of size 9.55 Å × 9.55 Å × 13.50 Å, and an external pressure of ~50 kbar was introduced.

3.2.1. Adsorption of the First H₂ on Solid C₆₀. Under the pressure of pressure of ~50 kbar, we explored the reactive trajectory of the first H₂ dissociative chemisorption on C₆₀ as shown in Figure 4. There are three steps involved: first, the incoming H₂ dissociation and deposition on two adjacent C₆₀, from structure U to V, through transition structures (TS 11); second, the rotation of C₆₀; and finally, hydrogen migration through TS 12 to structure W, a 1,2-addition product. Figure 5 gives the plot of the relative energies for the dissociative H₂ chemisorption on solid C₆₀. From this figure, we can see that the initial dissociative chemisorption step has a barrier of 1.36 eV, while the barrier for the subsequent H migration is much lower at 0.5 eV. Compared to adsorption barrier on single C₆₀ in gas phase, the barrier for H₂ molecules adsorption on two adjacent C₆₀ is quite low at 1.36 eV, which indicates that the reaction can easily take place at room temperature [16]. The energy barrier differences are mainly due to the rotation. In high pressure, C₆₀ does not stand in his own position quietly but rotates around the center of mass randomly. The rotation deforms the H–H bond to help break the H–H bond, which leads to lower reaction barrier.

In addition, we have made some comparison between the first H₂ chemisorption on solid C₆₀ and solid (6,6) armchair carbon nanotube. The barrier difference for initial chemisorption is 0.14 eV. And the barrier difference for the H atom migration is 0.38 eV. Both the barrier differences are small. From this table, we can conclude that, energetically, there are no significant differences between the chemisorption on solid C₆₀ and solid carbon nanotube under high pressure.

3.2.2. Adsorption of the Second H₂ on Solid C₆₀. To explore whether it is possible to chemisorb more H₂ on the solid C₆₀ under high pressure, we investigate the reaction path for the addition of the second H₂ on C₆₀ as shown in Figure 6. The reaction mechanism is quite similar to the addition of the first one. In this process, the second H₂ also dissociatively chemisorbs on two adjacent C₆₀ in the initial step and then rotates slightly; one of the H atom migrates from one C₆₀ to another and finally forms two 1,2-addition products. The relative energies for the chemisorption of second H₂ on solid C₆₀ were shown in Figure 7. Compared to the first H₂ chemisorption, the calculated barrier for the second H₂ is 1.21 eV in the dissociation step, which is a littler lower than that for the first H₂ adsorption. In addition, the overall process is also more exothermic, from 0.44 eV to 1.77 eV. This is mainly due to the fact that the first H₂ molecule adsorption has already partially disrupted the conjugated system, so further addition is much easier.

In the first H₂ adsorption process, we have mentioned that one of the H atoms will transfer from one C₆₀ radical to another. There is another probability that H₂ molecules react with the intermediate radical directly. We also investigate this kind of adsorption modes. For the C₆₀-H intermediate, there are two active sites: site 2 and site 4. There are three probable adsorption modes: (1,2)-(1,2) adsorption, (1,4)-(1,4) adsorption, and (1,2)-(1,4) adsorption. For (1,2)-(1,2) adsorption, it means one H atom is adsorbed in site 2 and another H atom is also adsorbed in site 2 (Figure 8). The rules also apply for both (1,2)-(1,4) adsorption and (1,4)-(1,4) adsorption. The barriers of three category reactions are listed in Table 2. From this table, we can see that all the barriers are no more than 0.8 eV. They are much lower than the formerly calculated barrier 1.21 eV. The overall exothermic energies are also a little larger than the former calculated exothermic energy 1.77 eV. Based on these data, a conclusion can be drawn that the subsequent H₂ molecules will easily react with C₆₀ intermediate radicals. Thus the reaction is a chain reaction: once the first H₂ is adsorbed, the H₂ will be adsorbed one by one. There is no extra energy needed because the overall exothermic energy will compensate the energy which is needed to overcome the barrier. Herein the first H₂ molecule adsorption has become the crucial step in the overall adsorption.
Figure 6: Optimized structures and transition state (TS) structures for the second H₂ dissociative chemisorption on C₆₀. Selective distances are given in Å.

Figure 7: Reaction profile for the second H₂, dissociative chemisorption on solid C₆₀. Energies are given in eV.

Figure 8: Adsorption modes for the second H₂ adsorption.

4. Conclusions

Based on the investigation of H₂ molecules chemisorption on fullerene C₆₀ and C₈₀ and endofullerene Sc₃C@C₈₀, we proposed a mechanism for H₂ molecules adsorption on solid C₆₀ under high pressure. Due to the rotation of C₆₀, the H₂ molecule will easily chemisorb on two adjacent C₆₀ under high pressure, which is more favorable than the H₂ molecule adsorption on single C₆₀. The overall reaction is a chain reaction. The first H₂ molecules adsorption is the crucial step in the overall H₂ molecules adsorption process. Once the first H₂ molecules is adsorbed on the C₆₀, the second and subsequent H₂ will easily be adsorbed on the C₆₀ due to the lower reaction barrier.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
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References


