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## Hydrogenation mechanism of small fullerene cages

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### ABSTRACT

Ab initio DFT (density functional theory) is used to investigate the hydrogenation energy and hydrogenation mechanism of  $C_n$  and  $C_nH_n$  fullerene cages from  $n = 20$  to  $n = 60$ . All calculations have been performed using G03W package, with B3LYP exchange-functional and applying basis set 6–31G(d, p). It is found that the most stable hydrogenation sites on the  $C_n$  fullerene cages are  $3V_5$  and  $5V_5$  sites and on the  $C_nH_n$  fullerene cages are  $6V_6$ ,  $6V_6$  and  $6V_5$  sites. The calculations show that the required energy to initiate the hydrogen migration on the surface of  $C_n$  fullerene cages between two metastable structures of  $C_{54}H$  is  $\sim 1.5$  eV and on the surface of  $C_nH_n$  fullerene cages between metastable and stable structures of the  $C_{60}H_{61}$  fullerene cage is  $\sim 2.35$  eV. Also, it is found that the energy release from hydrogen migration is always enough to direct the hydrogenation process towards the most stable structures and it reduces the number of hydrogen atoms bonded to the fullerene cage via forming  $H_2$  molecules.

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### Introduction

Many experimental and theoretical attempts are made for enhancement the hydrogen storage in carbon materials [1–10]. In particular, endohedral and exohedral hydrogen storage capacity of  $C_{60}$  and metal decorated  $C_{60}$  have been investigated using various experimental techniques and theoretical methods [11–15]. The hydrogen storage in many systems as  $Ti_6C_{24}B_{24}$  [16],  $C_{48}B_{12}M_{12}$  ( $M = Fe, Co, Ni$ ) [17],  $M_{32}B_{80}$  ( $M = Ca$  and  $Sc$ ) [18]  $Li_9C_{60}$  [19],  $Li_{12}C_{60}$  [20], Ti doped fullerene [21], fullerene-like  $Co_3C$  [22] Ni-dispersed fullerenes [23] sodium intercalated fullerenes [24]  $Be@C_{60}$  [25] have exhibited remarkable hydrogen adsorption capacity. Also, by the incorporation of C into  $(BN)_{12}$  fullerene [26,27] theoretical investigation shows that the hydrogenation reaction on carbon doped cluster is both thermodynamically favored and kinetically feasible under ambient.

Hydrogenated  $C_{60}$  fullerene cages were synthesized soon after the development of industrial methods to produce significant quantities of these materials [28–39]. Experimentally, hydrogenated  $C_{60}$  fullerene cages are synthesized by many methods as the direct non-catalytic hydrogenation, producing  $C_{60}H_{2-18}$  [40], the reaction of gaseous hydrogen with  $C_{60}Pd_{4,9}$ , producing  $C_{60}H_{2-26}$  [35], the catalytic hydrogenation in toluene solution in the presence of Ru/C, producing  $C_{60}H_{36-48}$  [41], the radical hydrogenation with promoter  $C_2H_5I$ , producing  $C_{60}H_{36}$  [42], the reduction with lithium in ammonia in the presence of BuOH, producing  $C_{60}H_{18-36}$  [33], the reduction in toluene solution through hydroborating or hydrozirconating producing  $C_{60}H_{2-4}$  [31], the hydrogen transfer on the fullerene from the dihydroanthracene, producing  $C_{60}H_{18-36}$  [43]. Also, the interaction of  $C_{60}$  with hydrogen atoms has also been intensively studied theoretically [44–47] showing that the theoretical predictions of the stability of hydrogenated fullerene cage  $C_{60}H_{60}$ .

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It is clear that the theoretical predictions of the hydrogenated fullerene cage of  $C_{60}H_{60}$  are always larger than the actual experimental production,  $C_{60}H_n$  ( $n < 60$ ). Also, the X-ray studies have shown that the hydrogenated fullerene cage  $C_{60}H_{36}$  is characterized by the molecular destruction caused by the break of bonds [32,46,48]. It should be emphasized that the experimental methods for hydrogenated fullerene cages have not yet to give the maximum hydrogen content for some unknown reasons. Therefore our main task in this paper is to clarify these unknown reasons.

One of the experimental studies has shown that the degree of hydrogenation and the mechanism of this process are related to the structure of the fullerene cages and, in particular, to the pentatomic rings forming the fullerene cages [49]. Hence, the small fullerene cages  $C_n$ ,  $n = 20$  to 60, are chosen to investigate the effect of pentatomic rings on the hydrogenation mechanism. All the possible hydrogenation sites inside and outside each fullerene cage from  $C_{60}$  cage to  $C_{20}$  cage are investigated. Also, the hydrogen migration energies between different hydrogenation sites are calculated.

## Methodology

All calculations are performed with DFT as implemented within G03W package [50–53], using B3LYP exchange-functional [54,55] and applying basis set 6–31G(d, p). All obtained structures are fully optimized where the  $C_n$  fullerene cages are optimized under symmetric constraint however  $C_nH$  and  $C_nH_{n+1}$  are optimized without any constraint. All the optimized geometric structures are confirmed with frequency calculations where all vibrational frequencies are found to be positive. In this work, the hydrogen adsorption energies of depositing one hydrogen atom on the  $C_n$  and  $C_nH_n$  fullerene cages from  $n = 20$  to  $n = 60$  are investigated. The hydrogen adsorption energy ( $E_{ads}^H$ ) is calculated as  $E_{ads}^H = E(C_{cage}-H) - (E(C_{cage}) + E(H))$  [56], where  $E(C_{cage}-H)$  the energy of hydrogenated cage,  $E(C_{cage})$  the energy of fullerene cage and  $E(H)$  the energy of a hydrogen atom. The energy barrier is calculated as the energy difference between the initial structure and the saddle point structure [57]. The saddle point structure is obtained by orthogonality constraints where all atoms is stepped a long a specified 3N vector (the difference between the relaxed initial and final structures) and allowed to relax at each step point in all directions orthogonal to this vector.

## Results

### Geometric structures

All the small fullerene cages are formed by two types of C–C bonds, a double bond character with average bond length 1.39 Å and a single bond character with average bond length 1.45 Å.  $C_{60}$  cage is a truncated icosahedron of the point-group symmetry (Ih) and sixty carbon atoms are arranged in 20 six-membered and 12 five-membered rings.  $C_{58}$  cage possesses a  $C_{3v}$  symmetry and fifty eight atoms are arranged in 17 six-membered, 13 five-membered and 1 seven-membered rings.  $C_{56}$  cage has  $D_2$  symmetry and fifty six atoms arranged in 18

six-membered and 12 five-membered rings.  $C_{54}$  cage has  $C_{2v}$  symmetry and fifty four atoms which are arranged in 16 six-membered and 12 five-membered rings.  $C_{52}$  cage possesses a  $C_2$  symmetry and fifty two atoms are arranged in 16 six-membered, and 12 five-membered rings.  $C_{50}$  cage has  $D_{5h}$  symmetry and fifty atoms arranged in 15 six-membered and 12 five-membered rings.  $C_{48}$  cage possesses  $D_3$  symmetry and forty eight atoms which are arranged in 14 six-membered and 12 five-membered rings.  $C_{46}$  cage has  $C_2$  symmetry and forty six atoms are arranged in 13 six-membered and 12 five-membered rings.  $C_{44}$  cage has  $D_{3h}$  symmetry and forty four atoms arranged in 12 six-membered and 12 five-membered rings.  $C_{42}$  cage possesses  $D_3$  symmetry and forty two atoms are arranged in 11 six-membered and 12 five-membered rings.  $C_{40}$  cage has  $D_2$  symmetry and forty atoms arranged in 10 six-membered and 12 five-membered rings. Finally,  $C_{20}$  cage is a truncated icosahedron of the point-group symmetry (Ih) and twenty carbon atoms are arranged in zero six-membered and 12 five-membered rings, see Fig. 1.

All the sixty carbon atoms of the  $C_{60}$  cage are equivalent, therefore, only one adsorbing site is present; namely  $\text{V}_6^6$  site, the vertex between two hexagons and one pentagon [58,59]. For the  $C_{58}$  cage, there are four different adsorption sites; namely  $\text{V}_6^6$  site (the vertex between two hexagons and one heptagon),  $\text{V}_5^6$  site (the vertex between one pentagon, one hexagon and one heptagon),  $\text{V}_5^5$  site (the vertex between two pentagons and one heptagon),  $\text{V}_5^6$  site (the vertex between two pentagons and one hexagon) and  $\text{V}_6^6$  site. For the rest of small fullerene cages, there are four different adsorbing sites; namely  $\text{V}_5^5$  site (the vertex between three pentagons),  $\text{V}_6^6$  site (the vertex between three hexagons), the  $\text{V}_5^5$  site and the  $\text{V}_6^6$  site, see Fig. 2.

### Hydrogen adsorption

#### First hydrogenation outside and inside the $C_n$ fullerene cages

The first hydrogenation (adsorption) energy outside and inside the small fullerene cages is calculated and is shown in Tables 1,2. All the adsorbed hydrogen atoms outside and inside the small fullerene cages are bonded to the carbon atoms with average bond length 1.1 Å. For outside hydrogenation, the bonds between the hydrogenated carbon atom and its first three neighbor carbon atoms are single bonds with average bond length 1.55 Å, 1.54 Å, 1.54 Å, 1.52 Å at  $\text{V}_6^6$  site,  $\text{V}_6^6$  site,  $\text{V}_5^5$  site and  $\text{V}_5^5$  site, respectively. Also, for inside hydrogenation the bonds between the hydrogenated carbon atom and its first three neighbor carbon atoms are single bonds with average bond length 1.50 Å, 1.50 Å, 1.48 Å, 1.50 Å at  $\text{V}_6^6$  site,  $\text{V}_6^6$  site,  $\text{V}_5^5$  site and  $\text{V}_5^5$  site, respectively. Therefore, one can report that the first hydrogen deposition atom outside and inside the  $C_n$  fullerene cage leads to convert all the bonds between the hydrogenated carbon atom and its first neighbor carbon atoms to single bonds, see Fig. 3. Also, it is noticed that the hydrogen deposition is accompanied by puckering the bonded carbon atom outside the surface of fullerene cages. This observation is reported previously [60] and leads to improve the stability of fullerene cages.

From Tables 1,2, the adsorption energy of the first hydrogenation outside the small fullerene cages is always lower than the adsorption energy inside the small fullerene cages. Also, it is found that the most stable hydrogenation sites are at  $\text{V}_5^5$  and  $\text{V}_6^6$  sites outside the surface of fullerene cages, agrees

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