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RESEARCH ARTICLE

DFT study of dihydrogen interactions with lithium containing organic complexes $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ (m = 1, 2)

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The interactions of dihydrogen with lithium containing organic complexes $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ (m = 1, 2) were studied by means of density functional theory (DFT) calculation. For all the complexes considered, each bonded lithium atom can adsorb up to five H_2 molecules with the mean binding energy of 0.59 eV/H_2 molecule. The interactions can be attributed to the charge transfer from the H_2 bonding orbitals to the Li 2s orbitals. The kinetic stability of these hydrogen-covered organolithium molecules is discussed in terms of the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The results indicate that these organiclithium structures can perhaps be used as building units for potential hydrogen storage materials.

Keywords adsorption, density functional calculations, organolithium molecule, hydrogen storage

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1 Introduction

The interaction between hydrogen and organometallic complexes has been a topic of great interest in hydrogen storage community for a long time. The US Department of Energy has set a target for the development of hydrogen storage technologies that the capacity should reach 9 wt% by weight hydrogen and volumetric capacity of 81 g·L^{-1} in 2015 for usable specific energy from H2 (net useful energy/max. system mass or volume) [1, 2]. As we know, many authors have paid more attentions on the hydrogen storage property of carbon nanotubes (CNTs) or boron nitrogen nanotubes (BNNTs) duo to the porous tube structure and large surface area of nanotube [3, 4], and also alkaline earth metal Ca was considered by some research groups [5–7]. Since subsequent studies have found that the nanotubes do not possess hydrogen storage capacity (HSC) as high as it is claimed [8, 9], the desired organometallic materials that can store hydrogen with high gravimetric and volumetric density and that can allow hydrogen adsorption and desorption to be operated under ambient conditions are investigated. In order to better understand the organometallic structures, some authors have carried out many experiments [10–15] in recent years that involve mass spectra, fragmentation channels, and electronic properties of transition and nontransition metal atoms interacting with different organic molecules. The key to finding organometallic materials that are ideal for hydrogen storage is not only to understand the interaction between hydrogen and host material but also the manner in which it can be altered.

Hydrogen is commonly known to interact with hydrogen storage materials in two ways, i.e., physisorption or chemisorption [16]. The binding energy of hydrogen in physisorption is of the order of a few meV, while in chemisorption is of the order of a few eV [17]. In the former case, storing molecular hydrogen by physisorption allows fast adsorption and desorption at ambient temperature and pressure condition. However, the main disadvantage is that hydrogen storage capacity is limited due to the low binding energy between H_2 and hydrogen storage materials. In the later case, molecular hydrogen is dissociated and adsorbed as atomic hydrogen on the host material. The main advantage is that higher HSC is achieved duo to the higher binding energy between the atomic H and host material. The main disadvantage is the poor kinetics in the hydrogen desorption.

An ideal situation is having the binding energy in the

intermediate region between physisorption or chemisorption [18]. This can be achieved by doping or introducing metal or charged sites, such as Li, Ca or transition metals (TM). These suggestions have been tested in various theoretical works and it has been shown in various works that binding energy exists in the desired range.

It was reported that Ti^+ cation could bind up to six H_2 molecules [19]. The first dihydrogen is chemisorbed as atomic hydrogen, while other dihydrogens are physisorbed as molecular hydrogen. Several groups found that Ti-decorated nanotubes [20], fullerenes [21], and ethylene molecules [22, 23] could serve as potential high capacity hydrogen storage materials.

Li^+ cations were found to be able to bind up to six H_2 molecules with a mean value of 4.77 kcal/mol [24]. Contrary to the Ti case, all the dihydrogens retain molecular form upon interaction with Li. Deng *et al.* proposed a new alkali-metal doped pillared carbon graphite or nanotubes storage material, which could adsorb H_2 at ambient temperature and pressure [25]. Similarly, Mpourmpakis *et al.* suggested that Li-doped carbon nanoscrolls could serve as potential hydrogen storage media [26]. In two other reports, Li or Na coated fullerenes could yield an approximate HSC of 9 wt% [27, 28]. Based on density functional theory (DFT) calculation, these authors found each Li/Na atom that is capped on the pentagonal or hexagonal face of fullerene molecule can adsorb up to five/six H_2, respectively. The advantage of lithium atoms over transition metal atoms is that the isolated form is preferred over clustering. Therefore, all metal sites remain active and can adsorb the maximum amount of H_2. In the work analogous to that with Ti, it was shown that an ethylene molecule could be decorated with up to two lithium atoms and a total number of four dihydrogen molecules [22]. Liu *et al.* found the adsorption capacity of $Li_2C_2H_4^+$ (27.5 wt%) is doubled compared with that of $Li_2C_2H_4$ [29]. In all these works, it was proposed that upon the interaction with organic materials, the lithium atoms lose charge and become positively charged. All these conclusions were supported by DFT calculations.

In this paper, we provide the results of a theoretical study of the interactions of H_2 molecules adsorbed on lithium containing organic complexes $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ (m = 1, 2). The optimized geometries of the organolithium molecules are presented in Fig. 1. The main difference between the structures proposed here and the counterparts in the previous works is that lithium atoms are not dopants but constitute parts of the molecules on the plane of C_nH_n (n = 4, 5). In the following a detailed study of adsorption process will be presented. In addition to achieving a fundamental understanding of the interactions between H_2 molecules and organolithium complexes, the results may shed light on their potential applications for hydrogen storage.

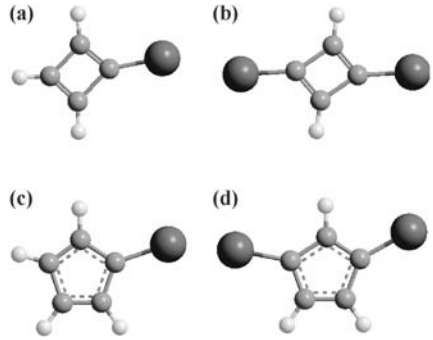

Fig. 1 Basic optimized geometries of $C_nH_{n-m}Li_m$ (n = 4, 5; m = 1, 2). Gray: carbon; white: hydrogen; dark gray: lithium.

2 Computational methods

DFT using the B3LYP [30, 31] method with 6-31G(d, p) basis set was employed to optimize the ground state of all molecular systems considered here. Vibrational frequency calculations were carried out for each optimized structure to verify the reasonability of optimized structure. The energy obtained was corrected by basis set superposition error (BSSE) by means of the counterpoise technique of Boys and Bernardi [32]. The mean binding energy per H_2 under same p in $C_nH_{n-m}Li_m$-$m(pH_2)$ (n = 4, 5; m = 1, 2; p = 1–5) was calculated using formula (1):

$$\Delta E_p = \{E[C_nH_{n-m}Li_m\text{-}m(p-1)H_2] + mE[H_2] - E[C_nH_{n-m}Li_m\text{-}mpH_2]\}/m \quad (1)$$

The mean binding energy per H_2 under same m in $C_nH_{n-m}Li_m$-$m(5H_2)$ (n = 4, 5; m = 1, 2) was calculated using formula (2):

$$\Delta E = \{E[C_nH_{n-m}Li_m] + 5mE[H_2] - E[C_nH_{n-m}Li_m\text{-}m(5H_2)]\}/(5m) \quad (2)$$

The HOMO–LUMO energy gap was calculated to verify the kinetic stability of all molecular systems. All calculations were performed using Gaussian 03 programs [33].

3 Results and discussion

The optimized geometries of $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ (m = 1, 2) are shown in Fig. 1. As shown in Fig. 1, the structures of lithium containing the organic complexes under study can be formed by substituting H atoms for Li atoms on the C_nH_n plane. The Li atoms are located on σ_h plane of C_nH_n molecule, far from the structures that metal atoms are situated on the n-fold symmetry axis of C_nH_n [34–36]. We select only m = 1, 2 for $C_4H_{4-m}Li_m$, $C_5H_{5-m}Li_m$ in respect that more Li atoms in $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ (m = 1, 2) cannot exhibit as good hydrogen adsorption property as

the case of $n = 1, 2$. At the same time, other isomers also own poor hydrogen adsorption property. In the following, we study the H_2 interactions with organolithium complexes $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ ($m = 1, 2$).

We first start with the optimized geometries of C_5H_4Li-$p H_2$ as a function of p, as shown in Fig. 2. The first H_2 molecule may be adsorbed over the Li atom in many different orientations, either on the same plane as the C_5H_5 derivatives or out of the plane. However, the structure with a C_{2v}-symmetric out-of-plane is a minimum according to the DFT. Each hydrogen atom is 2.17 Å to Li atom and the H–H axis is perpendicular to the C_5H_5 plane, as depicted in Fig. 2(a). When the second H_2 molecule is adsorbed, the two H_2 molecules take side-on positions with respect to the Li atom on the opposite sides of the C_5H_5 plane, as presented in Fig. 2(b). The optimized structures are not purely T-shaped. The hydrogen atoms are located at 2.15 Å and 2.22 Å away from the Li atom. In the presence of three/four adsorbed H_2 molecules, a triangular/square pattern is formed. Again, the H_2 molecules take side-on positions with respect to the Li atom and the asymmetric T-shaped patterns are formed. However, as can be seen in Fig. 2(e), the fifth H_2 molecule is situated outside the plane defined by the foregoing four H_2 molecules. The last H_2 molecule is less bound than other four H_2 molecules. Each hydrogen atom of the fifth H_2 molecule is located at 2.45 Å away from the Li atom. When the sixth H_2 is added, no stable structure can be got, so no more H_2 molecules can be adsorbed.

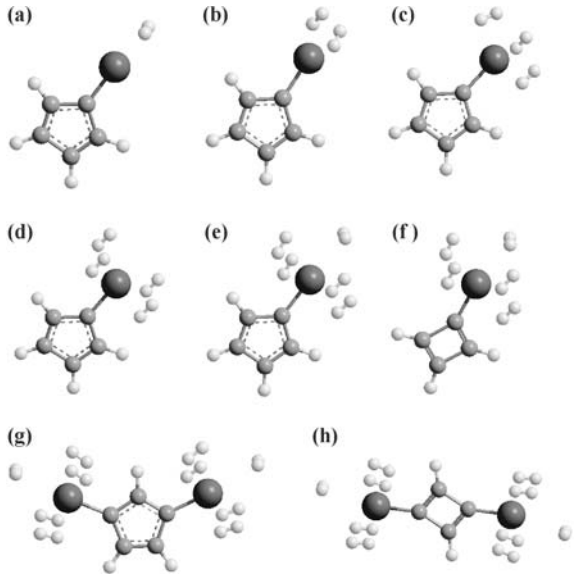

Fig. 2 Basic optimized geometries of C_5H_4Li-(pH_2) (p = 1–5) and $C_5H_3Li_2$-2($5H_2$) $C_4H_{4-m}Li_m$-m($5H_2$) ($m = 1, 2$). Gray: carbon; white: hydrogen; dark gray: lithium.

The hydrogen adsorption by other complexes C_4H_3Li, $C_4H_2Li_2$, and $C_5H_3Li_2$ are similar to that of C_4H_3Li-pH_2 (p = 1–5) and we will not describe them one by one. We only give the optimized geometries of $C_nH_{n-m}Li_m$-m ($5H_2$) ($n = 4, 5$; $m = 1, 2$) in Fig. 2. Each lithium atom of the complexes $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ (m = 1, 2) can adsorb five H_2 molecules at the maximum and all H_2 molecules take side-on positions with respect to lithium atoms. In addition, the effect of BSSE correction during the optimization is not important for these complexes. The mean binding energy per H_2 molecule was calculated by formula (1) and (2). The results are presented in Table 1 from which one can find all the calculated binding energies for per H_2 are in the intermediate region between physisorption or chemisorption, so they all allow fast hydrogen adsorption and desorption under ambient thermodynamic condition.

Table 1 The mean binding energy ΔE_m (eV) per H_2 under same p of and mean binding energy ΔE (eV) per H_2 under same m of $C_nH_{n-m}Li_m$-m (pH_2).

		ΔE_p	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	ΔE
$C_4H_{4-m}Li_m$	$m = 1$	0.64	0.61	0.59	0.55	0.55	0.59
-m (pH_2)	$m = 2$	0.63	0.61	0.58	0.55	0.54	0.58
$C_5H_{5-m}Li_m$	$m = 1$	0.63	0.6	0.6	0.56	0.55	0.59
-m (pH_2)	$m = 2$	0.62	0.59	0.6	0.57	0.54	0.59

It is well known that the kinetic stability of a molecular system is governed by the energy gap between the highest occupied orbit and lowest unoccupied orbit. The larger the gap, the more steady the system is. We have plotted the HOMO–LUMO gaps of the above hydrogen-decorated lithium containing organic systems as a function of p in Fig. 3. As we can see in Fig. 3, under the same m, the HOMO–LUMO gaps for $C_nH_{n-m}Li_m$-m(pH_2) rise as the number of hydrogen molecule increases and reach the maximum at $p = 5$ with a little welter during

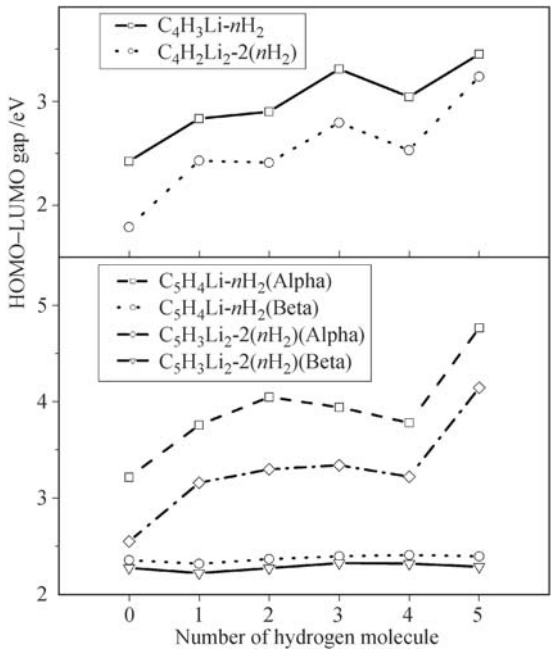

Fig. 3 The HOMO–LUMO energy gap for complexes $C_nH_{n-m}Li_m$-m(pH_2) (n = 4, 5; m = 1, 2; p = 1–5) as H_2 molecules are added successively.

the process. This reflects that all the lithium containing the organic complexes under study own excellent kinetic stability, which is propitious to hydrogen storage.

The interactions between H_2 and lithium containing organic molecules can be attributed to electrostatic forces. The electrostatic field around the Li atom originates from the charge transfer from Li to the organic molecule. The mean Milliken charge per Li atom of $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ ($m = 1, 2$) as H_2 molecules are added successively are shown in Table 2. The Li atoms in the $C_nH_{n-m}Li_m$ are found to be positively charged due to the donation of electronic charge from Li 2s orbital to the C_n ring. When the H_2 molecules are adsorbed successively, the charge is transferred from H_2 bonding orbital to Li 2s orbital. Through the charge transfer the electrostatic forces are caused, and accordingly these molecular systems are combined stably. The same effect has been reported in previous work, in which the electrostatic interactions between dihydrogen and alkali–metal cations are studied [37]. The HOMO, LUMO surfaces and the HOMO, LUMO charge density surfaces of $C_4H_2Li_2$-2($5H_2$) $C_5H_3Li_2$-2($5H_2$) which own the highest HSM corresponding to C_nH_n ($n = 4, 5$) are shown in Fig. 4.

Table 2 The Mulliken charges (a.u) for lithium metal atom in $C_nH_{n-m}Li_m$-m ($p H_2$) ($n = 4, 5$; $m = 1, 2$; $p = 1$–5).

	p	$p=0$	$p=1$	$p=2$	$p=3$	$p=4$	$p=5$
$C_4H_{4-m}Li_m$	$m=1$	0.33	0.23	0.16	0.09	0.05	0.03
-m (pH_2)	$m=2$	0.24	0.15	0.09	0.03	–0.01	–0.03
$C_5H_{5-m}Li_m$	$m=1$	0.38	0.3	0.23	0.13	0.08	0.05
-m (pH_2)	$m=2$	0.29	0.25	0.14	0.07	0.02	0.01

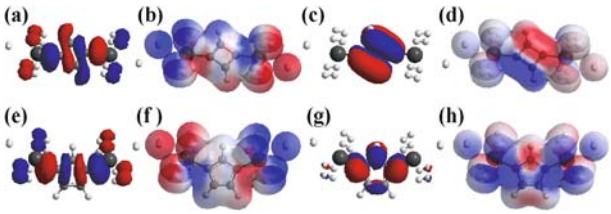

Fig. 4 The HOMO, LUMO surface and HOMO, LUMO charge density surface of $C_4H_2Li_2$-2($5H_2$) and $C_5H_3Li_2$-2($5H_2$). The first column to fourth column are corresponding to HOMO, HOMO charge density surface, LUMO and LUMO charge density surface, respectively.

Based on the results and discussions above, it is found that the complex $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ ($m = 1$, 2) studied here owns excellent hydrogen adsorption character and exhibits excellent kinetics stability. The HSM predicted is 14.70–23.80 wt% for $C_4H_{4-m}Li_m$, 12.34–20.61 wt% for $C_5H_{5-m}Li_m$, respectively. All the vibrational frequencies for these molecular systems are positive, which indicates that the systems are actually situated at the local minima in their potential energy surfaces. Therefore, the lithium containing organic complexes here may be useful for hydrogen storage.

4 Summary and conclusions

In the present paper, we have made a systematic study of hydrogen adsorption based on organolithium complexes $C_4H_{4-m}Li_m$ and $C_5H_{5-m}Li_m$ ($m = 1, 2$). The DFT calculations testify that each lithium atom of $C_nH_{n-m}Li_m$ can absorb strongly up to five H_2 molecules in between physisorption and chemisorption. The highest HSM obtained is 23.80 wt%. Hence these complexes can serve as building units for potential hydrogen storage medium. Further studies on the reactive kinetics of the process are necessary. Meanwhile, since organo–metallic complexes are molecules, not materials, and cannot serve as hydrogen storage materials directly, building bulk materials on the basis of these molecules is important, such as metal–organic frameworks (MOFs) and covalence–organic frameworks (COFs) [38]. We are focusing on this in our current research [39].

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