Journal of Alloys and Compounds 509S (2011) S868–S871

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Nuclear quantum effect on hydrogen adsorption site of zeolite-templated carbon model using path integral molecular dynamics

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ARTICLE INFO

Article history:
Received 22 July 2010
Received in revised form
29 September 2010
Accepted 16 October 2010
Available online 23 October 2010

Keywords:
Carbon material
Zeolite-templated carbon
Nuclear quantum effect

ABSTRACT

To settle the hydrogen adsorption sites on buckybowl $C_{36}H_{12}$, which is picked up from zeolite-templated carbon (ZTC), we have performed path integral molecular dynamics (PIMD) simulation including thermal and nuclear quantum fluctuations under semi-empirical PM3 method. In the static PM3 calculation and classical simulation the five stable adsorption sites of hydrogen atom are optimized inside a buckybowl $C_{36}H_{12}$, which are labeled as α-, β_1-, β_2-, γ-, and δ-carbons from edge to innermost carbon. In PIMD simulation, meanwhile, stable adsorption site is not appeared on δ-carbon, but on only α-, β_1-, β_2-, and γ-carbons. This result is due to the fact that the adsorbed hydrogen atom can easily go over the barrier for hydrogen transferring from δ- to β_1-carbons by thermal and nuclear quantum fluctuations. The thermal and nuclear quantum effects are key role to settle the hydrogen adsorption sites on carbon materials.

1. Introduction

Carbon materials with large surface area, such as activated carbons, carbon nanotubes, and zeolite-templated carbon (ZTC), have attracted attention as hydrogen storage materials [1–6]. Among them, ZTC synthesized using zeolite Y as a template has some structural features of a buckybowl-like curved nanographene structure and uniform micropores [3–6]. Recently, we have succeeded to achieve the hydrogen storage in ZTC up to 2.2 wt%, which is the highest among any pure carbon materials [6], at 34 MPa at 303 K. There have also some attempts for enhancement of the hydrogen storage amounts, to apply the synthesizing structural isomer, adjusting pore size, and adding Pt nanoparticles [5,6]. Especially, it has been found that hydrogen storage amount of Pt-loaded ZTC increases compared with that of un-loaded one due to the effect of hydrogen spillover [6]. However, hydrogen storage amounts of these ZTC have not been satisfied from the view points of the practical use, yet. The elucidation of the detailed mechanism of diffusion process for spilled-over hydrogen atom on carbon surface and its adsorption sites is indispensable for the improvement of the hydrogen capacity.

From theoretical calculation, there have been many reports on the structure for hydrogen adsorption site on carbon materials, where carbon frameworks have been graphene-sheet, nanotubes, and fullerene types [7–10]. Recently, we have reported hydrogen adsorption site on buckybowl $C_{36}H_{12}$, as a fragment of ZTC, and found that the adsorption site of the additional hydrogen atom at out side of buckybowl is more stable than that at edges [11].

We address here that the previous theoretical studies have been based on the *ab initio* molecular orbital (MO) or molecular dynamics (MD) calculations, where quantum fluctuations of nuclei are completely neglected. However, it is known that the framework structure in the system is often affected by the thermal and quantum fluctuations due to the high anharmonicity or low frequency motions. Actually, we have already found that the nuclear quantum effect is significant in the case of hydrogen-bonded systems, where hydrogen atom plays an important role [12–14]. To settle the hydrogen adsorption sites on carbon materials such as ZTC, thermal and quantum fluctuations should be indispensable.

For detailed evaluating the additional hydrogen atom adsorption site on ZTC, we have performed the path integral molecular dynamics (PIMD) simulation [15,16], which can treat both thermal and quantum fluctuations. In the following section, we describe the computational method. In Section 3, the results and discussion for thermal and nuclear quantum effects on hydrogen atom adsorption sites of buckybowl $C_{36}H_{12}$ are shown. Finally, some concluding remarks are given in Section 4.

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doi:10.1016/j.jallcom.2010.10.066

2. Computational method

Buckybowl $C_{36}H_{12}$, which is the minimum unit of ZTC and includes three pentagonal carbons, was employed as a model structure [5,11]. The semi-empirical PM3 method was used for static MO calculation, conventional classical MD, and PIMD simulations with Gaussian03 program package [17]. We note here that the semi-empirical PM3 method has been already widely used for such hydrocarbon systems with static MO calculation, classical, and quantum simulations [18–21], and succeeded to reproduce experimental structures and enthalpies of formations. Based on such previous works, we have performed PIMD simulation including both thermal and nuclear quantum effects under the PM3 potential. The PIMD simulations were performed at 300 K with massive Nosé-Hoover thermostat algorithm using normal mode transformation [22–25]. All PIMD simulations were done with the imaginary time slices $P = 24$ (i.e., number of beads). Potential energy and its gradient vector are evaluated at each step. Apart from the "quantum simulation" by PIMD calculations, the "classical simulation" was also performed with $P = 1$ condition, which corresponds to conventional MD.

Fig. 1 shows equilibrium structure of $C_{36}H_{12}$ for (a) side of view and (b) top of view. Five carbons inside of buckybowl were selected for the hydrogen adsorption sites of additional hydrogen atom and labeled as "α-carbon", "β_1-carbon", "β_2-carbon", "γ-carbon", and "δ-carbon", respectively. Five optimized structures which were obtained by adding one hydrogen atom to α-, β_1-, β_2-, γ-, and δ-carbon on $C_{36}H_{12}$ have been used as initial configurations for both classical and quantum simulations. The length of simulations were 50 000 and 300 000 steps for PIMD and classical simulations, respectively. For convenience, the additional hydrogen atom is labeled as "H*".

Fig. 2 shows representative snapshot of $C_{36}H_{13}$ with H* adsorbing on β_2-carbon (a) in classical simulation and (b) in quantum simulation at 300 K.

3. Results and discussion

3.1. Static results

Table 1 lists binding energies for each optimized structure by PM3 level of calculation, as the preliminary results. The binding energy (ΔE) is defined as

$$\Delta E = (E_{C_{36}H_{12}} + E_{H}) - E_{C_{36}H_{13}}, \quad (1)$$

where Ex refers to the energy of species X. Table 1 clearly shows that the stable hydrogen adsorption sites are found in all five cases and the binding energy becomes larger as adsorption site change from innermost (δ-) to edge (α-) carbons. This tendency means that carbon framework at the edge is likely to be sp^3 character, more than that in innermost.

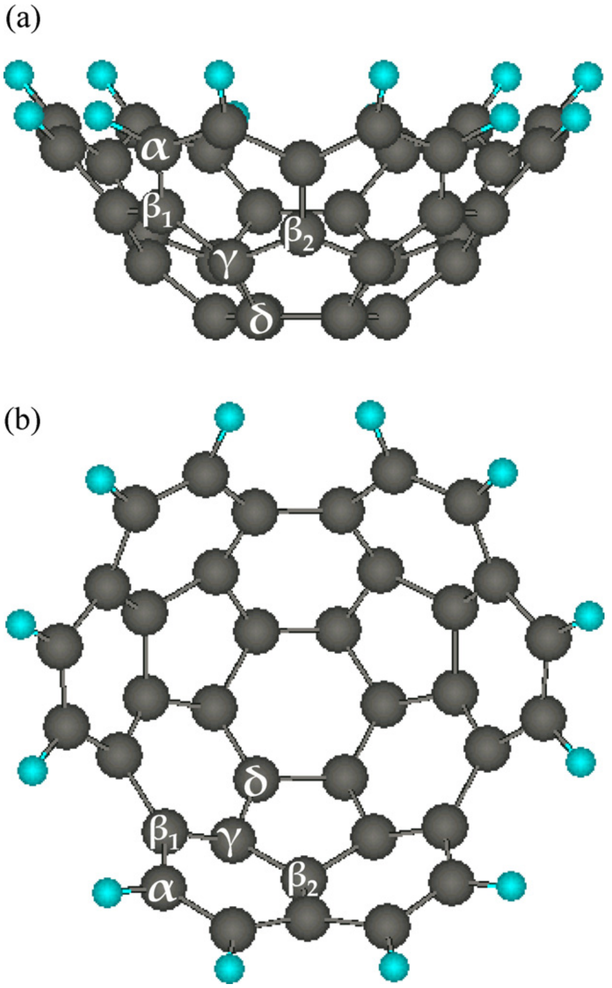

Fig. 1. Equilibrium structure of $C_{36}H_{12}$ at (a) side-view and (b) top-view.

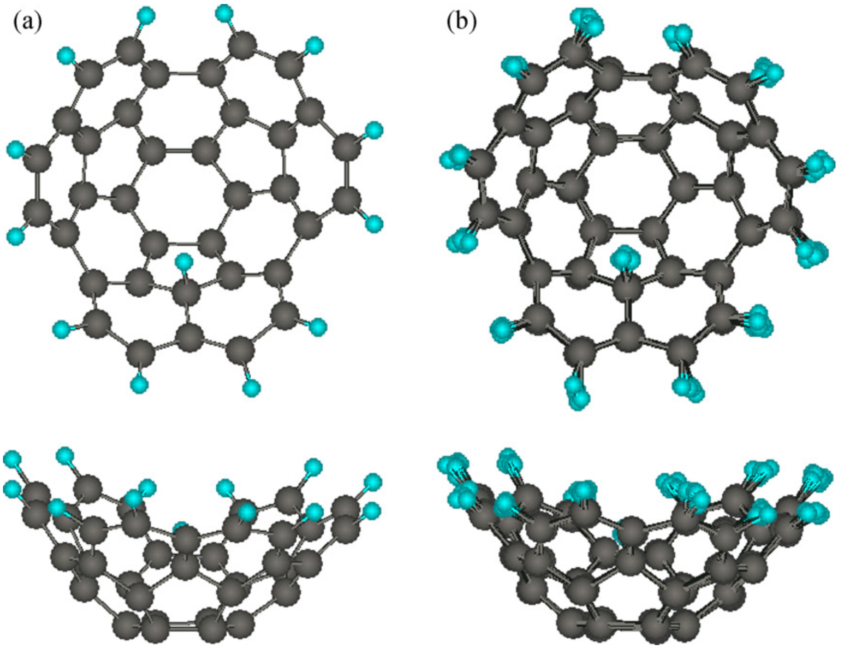

Fig. 2. Representative snapshot of $C_{36}H_{13}$ with H* adsorbing on β_2-carbon in (a) classical simulation and (b) quantum simulation at 300 K.

Table 1
Binding energies of $C_{36}H_{12}$. Units in kcal/mol.

	α-Carbon	β_1-Carbon	β_2-Carbon	γ-Carbon	δ-Carbon
ΔE	60.4	31.2	18.3	16.9	4.1
ΔE (with ZPE correction)	60.6	32.1	19.7	17.7	4.6

The binding energy with harmonic zero point energy correction is more stable than that without correction, despite degree of freedom of $C_{36}H_{13}$ is larger than that of $C_{36}H_{12}$ and H. This result means that $C_{36}H_{13}$ has more low frequency vibrational modes than $C_{36}H_{12}$ within the harmonic vibrational approximation. We again address here that H* can adsorb on every carbon at 0 K in the static MO calculation.

3.2. Classical simulation

Fig. 3 shows the one-dimensional distribution as a function of *R*, which is defined as the distance between H* and centroid of innermost hexagonal carbons. The *R* in the static MO calculations are 5.55 Å, 3.52 Å, 3.07 Å, 2.53 Å, and 1.55 Å for α-, β_1-, β_2-, γ-, and δ-carbon, respectively.

First, it can be seen that the adsorption sites of H* in classical simulations are appeared on every carbon atoms. The peak positions in classical simulations are found near the equilibrium ones by the static MO calculation. These results mean that H* in classical simulation is fluctuating near the each carbon by thermal effect under the anharmonic potential. It is found that hydrogen adsorption sites in classical simulation at 300 K are the almost similar as those by MO calculations.

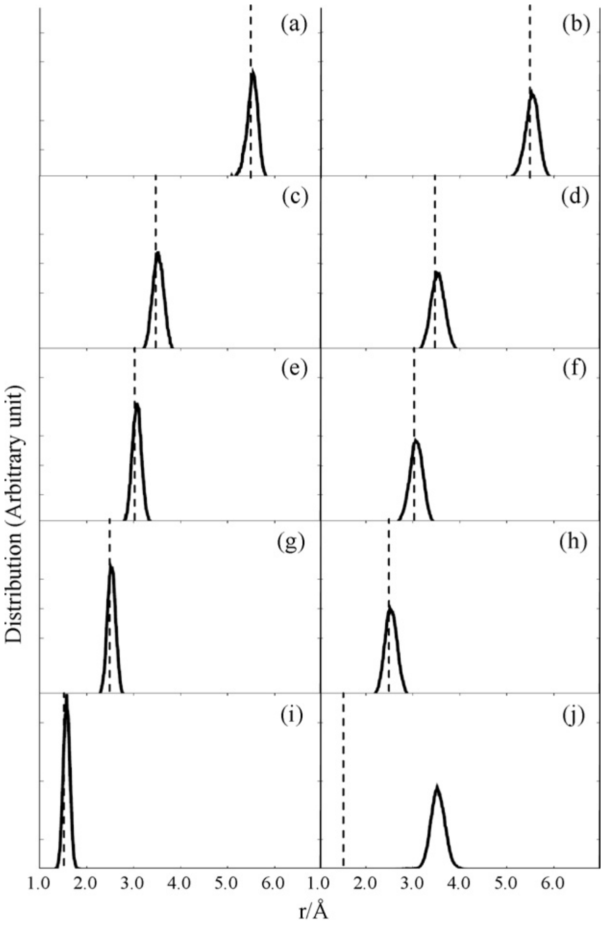

Fig. 3. One-dimensional distribution of *R* on classical (left side) and quantum (right side) simulations. Note that initial configurations of additional hydrogen adsorption site for (a and b), (c and d), (e and f), (g and h), and (i and j) are on α-, β_1-, β_2-, γ-, and δ-carbon, respectively.

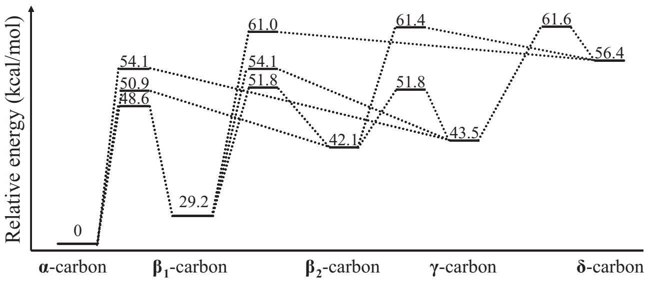

Fig. 4. Potential energy diagram of adsorbed hydrogen atom (H*) from one to other carbon without zero point energy correction.

3.3. Quantum simulation

Next, we discuss the result of quantum simulation. It is found that results in quantum simulation are almost same as that in classical one, excepted Fig. 3j. The distributions in quantum simulation are more delocalized than that in classical one due to the thermal and nuclear quantum fluctuations under the anharmonic potential. Surprisingly, Fig. 3j shows that distribution is not appeared near the δ-carbon but around the β_1-carbon. This result is quite different from the classical simulation and the static MO calculation. To discuss why H* adsorption site on δ-carbon is not appeared, we analyze energy diagram with respect to the H* transferring from one carbon to another carbon under harmonic vibrational frequencies. Here, harmonic vibrational CH* stretching modes for α-, β_1-, β_2-, γ-, and δ-carbons are 2989 cm^{-1}, 2647 cm^{-1}, 2543 cm^{-1}, 2533 cm^{-1}, and 2354 cm^{-1}, respectively.

Fig. 4 shows potential energy diagram of H* transferring from one carbon to the other carbon without zero point energy correction. Each transition state structure was obtained by quadratic synchronous transit (QST) approach [26,27]. It is found that energy barrier between δ-carbon and β_1-carbon is about 4.6 kcal/mol, which is the smallest among all paths. From harmonic vibrational analysis, it is found that H* is likely to go over the potential barrier between δ- to β_1-carbon due to the zero point vibration of CH* stretching and other low frequency modes as well as the thermal effect. On the other hand, the H* transferring from α-, β_1-, β_2-, and γ-carbon to other carbon is hard to occur at 300 K, since potential barriers in those paths are more than 3 kcal/mol higher than that from δ- to other carbon. Thus, distribution of H* around the δ-carbon is not appeared in quantum simulation.

4. Conclusions

We have performed the path integral molecular dynamics (PIMD) to settle the hydrogen adsorption sites on ZTC model. Stable hydrogen adsorption sites have been found on each carbon in the conventional static MO calculation and the classical simulation at 300 K, while those in PIMD simulation have been on only α-, β_1-, β_2-, and γ-carbons. Because of thermal and nuclear quantum effects, adsorbed hydrogen atom can easily go over the potential barrier between δ- and β_1-carbon. It is concluded that both thermal and nuclear quantum fluctuations are indispensable to evaluate the hydrogen adsorption site for carbon materials.

Acknowledgements

K. S., M. T., and U. N. thank to Dr M. Shiga at the Japan Atomic Energy Agency (JAEA) for useful discussions. This work has been supported by New Energy and Industrial Technology Development Organization (NEDO) under “Advanced Fundamental Research Project on Hydrogen Storage Materials”.

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