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REGULAR ARTICLE

Isotope effect of proton and deuteron adsorption site on zeolite-templated carbon using path integral molecular dynamics

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Abstract To analyze the proton/deuteron (H/D) isotope effect on the stable adsorption sites on zeolite-templated carbon (ZTC), we have performed path integral molecular dynamics simulations including thermal and nuclear quantum effects with the semi-empirical PM3 potential at 300 K. Here, for the adsorption sites of additional proton (H*) and deuteron (D*), we chose different five carbon atoms labeled as α-, β_1-, β_2-, γ-, and δ-carbons from edge to bottom for inside of buckybowl ($C_{36}H_{12}$ and $C_{36}D_{12}$). The stable adsorption sites of D* are observed on all carbon atoms, while those of H* are not observed on δ-carbon atom, but only on α-, β_1-, β_2-, and γ-carbon atoms. This result is explained by the fact that H* can easily go over the barrier height for hydrogen transferring from δ- to β_2-carbons at 300 K, since the zero-point energy of H* is greater than that of D*.

Keywords Carbon material · Nuclear quantum effect · Isotope effect

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 [1–7]. 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 managed to achieve the hydrogen storage in ZTC up to 2.2 wt% by molecular physisorption, which is the highest among any pure carbon materials [6], at 34 MPa at 303 K.

There have been also some attempts for the enhancement of the hydrogen-storage capacity, 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 the un-loaded ones due to the physisorption and chemisorption which is forming C–H bond [6]. However, the hydrogen-storage amounts of these ZTC have not yet been satisfied from the viewpoint of the practical use. The elucidation of the mechanism of hydrogen on carbon surfaces and stability of the adsorption sites for atomic and molecular hydrogen is indispensable for the improvement of the hydrogen-storage capacity.

There have been many reports on the H/D isotope effect to analyze the adsorption character and mechanism of H_2 and D_2 molecules on some carbon materials, such as carbon nanohorns, activated and porous carbons [8–10]. It has been observed that the total amount of adsorption of H_2 molecules is smaller than that of D_2 at low temperature.

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However, the isotope effect on the total amount of both adsorption and desorption of ZTC materials is not yet sufficiently known by both experimental and theoretical techniques.

There have been some theoretical studies concerning the nuclear quantum effect on hydrogen-storage materials [8, 11, 12] and discussion about H/D isotope effect [8, 13–15]. These works have focused on H_2 or D_2 storage on carbon materials due to the physisorption. Recently, on the other hand, we have reported stable or unstable atomic hydrogen chemisorption sites on buckybowl $C_{36}H_{12}$, which is a fragment of ZTC, by path integral molecular dynamics (PIMD) simulations including thermal and nuclear quantum effects [16, 17]. We found that the stable adsorption site for the additional atomic hydrogen inside of $C_{36}H_{12}$ exists on all carbon atoms, and the binding energy becomes greater as the adsorption site changes from the innermost to edge carbons by static molecular orbital (MO) calculations. From PIMD simulations, meanwhile, stable adsorption sites have not been observed on the positions of the innermost carbon atoms at 300 K due to the zero-point energy and thermal effects. We concluded that thermal and nuclear quantum effects are important for the theoretical analysis of hydrogen adsorption even at 300 K. However, in our previous works, we have only investigated for the stable or unstable adsorption sites of H species on ZTC at 300 K.

In this article, thus, we will investigate for the isotope effect of stable chemisorption sites for additional protons and deuterons on ZTC material by PIMD simulation at 300 K. In the following section, we give a brief description of the computational details, and results and discussion for isotope effects on stable or unstable adsorption sites of buckybowl $C_{36}H_{12}$ and $C_{36}D_{12}$ are shown in Sect. 3. Finally, some concluding remarks are given in Sect. 4.

2 Computational detail

A buckybowl-like molecule ($C_{36}H_{12}$ and $C_{36}D_{12}$), which is a basic building block of ZTC with the hydrogens terminated, was employed as a model structure [5, 16–18]. The semi-empirical PM3 method was used for static MO calculations and path integral molecular dynamics (PIMD) simulations with the Gaussian03 program package [19, 20]. We note here that the semi-empirical PM3 method has been already widely used for such hydrocarbon systems with static MO calculations, conventional and PIMD simulations [21–24], and managed to reproduce experimental structures and enthalpies of formations. Based on such previous works, we have performed static MO calculations and PIMD simulations including both thermal and nuclear quantum effects with the PM3 potential. Transition state structures are calculated using quadratic synchronous transit (QST) approach [25, 26]. To elucidate the isotope effects of stable and unstable adsorption sites for additional protons and deuterons to the ZTC, we have performed PIMD simulations, which can include both thermal and nuclear quantum effects [27, 28]. The PIMD simulations have been done at 300 K with massive Nosé–Hoover thermostat algorithm using normal mode transformation [29–32]. All PIMD simulations for the $C_{36}H_{13}$ and $C_{36}D_{13}$ consisted of 50 000 steps with the imaginary time of slices $p = 24$.

The equilibrium structure of $C_{36}H_{12}$ is shown in Fig. 1; (a) top of view and (b) side of view. Five carbon atoms of buckybowl molecule were selected for the adsorption sites of additional protons or deuterons, and each carbon was labeled as "α-carbon", "β_1-carbon", "β_2-carbon", "γ-carbon", and "δ-carbon", respectively, as shown in Fig. 1b. The optimized structures after adding a hydrogen atom to α-, β_1-, β_2-, γ-, and δ-carbons on the inside of $C_{36}H_{12}$ by static MO calculations have been used as the initial configurations for the PIMD simulations. For convenience, hereafter, the additional protons and deuterons are labeled as "H*" and "D*", respectively. The "R" is defined by the distance between additional H* and D* atoms and centroid of the innermost of

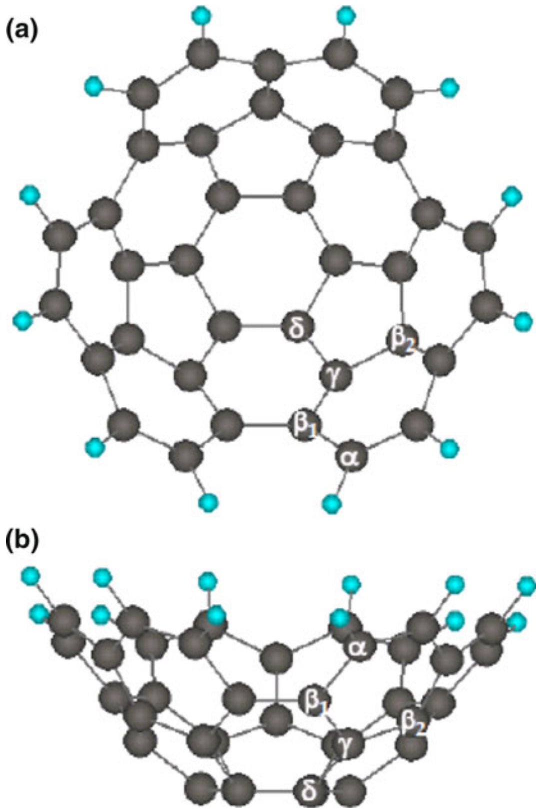

Fig. 1 Equilibrium structure of $C_{36}H_{12}$ at **a** top view and **b** side view

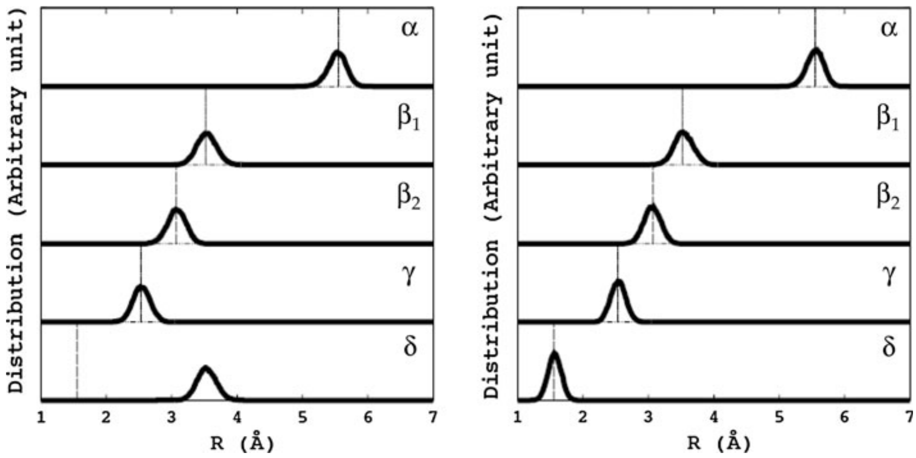

Fig. 2 One-dimensional distribution of *R* on $C_{36}H_{13}$ (*left side*) and $C_{36}D_{13}$ (*right side*) buckybowl structures. Note that initial configurations of additional H* or D* for each simulation are denoted as α, β_1, β_2, γ, and δ

the hexagonal carbons that are constructed from six equivalent δ-carbons.

3 Results and discussion

The one-dimensional distributions as a function of *R* are shown in Fig. 2. From previous calculations [16, 17], stable adsorption sites by static MO calculations have been observed at each carbon. Here, the *R* for α-, β_1-, β_2-, γ-, and δ-carbons by static MO calculations are shown as vertical dot line.

In Fig. 2, the distribution of H* is a little more broadened than that of D*. This result means that structural fluctuation of $C_{36}H_{13}$ is larger than that of $C_{36}D_{13}$ due to the difference of zero-point energy. The peak positions of H* have been observed at each α-, β_1-, β_2-, and γ-carbons, but not on δ-carbon due to the zero-point vibrational energy and thermal effects [16, 17]. On the other hand, the peak positions of $C_{36}D_{13}$ are observed at near all equilibrium positions. These results are similar results of static MO calculations.

To analyze the difference for stable adsorption site of H* and D*, the energy diagram of H* transferring from one carbon to another carbon on $C_{36}H_{12}$ is shown in Fig. 3. We have also carried out the harmonic vibrational analysis, in which the harmonic vibrational frequency of CH* (CD*) stretching modes for α-, β_1-, β_2-, γ-, and δ-carbons are 2,989 (2,172), 2,647 (1,940), 2,543 (1,859), 2,533 (1,853), and 2,354 (1,728) cm^{-1}, respectively.

The potential barrier from δ- to β_1-carbon atoms is 19 kJ/mol, which is the smallest among all paths in Fig. 3. From harmonic vibrational analysis, zero-point vibrational energy of the stretching mode between δ-carbon and H* and D* are 14 and 10 kJ/mol, respectively. It is found that H* is more likely to go over this potential barrier from δ- to β_1-carbon than D* due to the energy difference of zero-point vibration as well as thermal effects. Thus, isotope effects observed for the stable adsorption sites are caused by mainly the difference of zero-point vibrational modes.

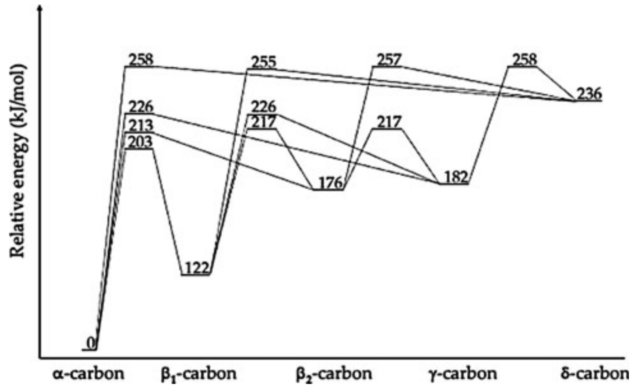

Fig. 3 Potential energy diagram of adsorbed hydrogen atom (H*) transferring from one to other carbon for inside of buckybowl. The unit is in kJ/mol

4 Conclusions

We have performed path integral molecular dynamics simulations at 300 K to analyze the isotope effect of stable adsorption site for additional proton (H*) and deuteron (D*) on zeolite-templated carbon (ZTC). The stable adsorption sites for H* are observed on all carbon atoms, except for the δ-carbon that is the innermost carbon inside of buckybowl, while those for D* are observed for each carbon. This is due to the fact that quantum effects of H* are larger than those of D*. Thus, our result suggests that the total amount of adsorption for D_2 is larger than those for H_2, since D* has more stable adsorption sites than H*.

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