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Effect of electric field on adsorption of formaldehyde by β-cellobiose in micro-scale

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ABSTRACT

To provide a microcosmic theoretical support for the reduction of formaldehyde in building material by the effect of electric fields, the adsorption between formaldehyde molecule and β-cellobiose was studied by density function theory (DFT). Details of geometric structures, molecule bonds and adsorption energy were discussed respectively. The obtained results indicated the energy of formaldehyde molecule decreased while the energy of β-cellobiose increased with greater electric intensity. In addition, the adsorption energy between formaldehyde molecule and β-cellobiose was greatly influenced by external electric field. The adsorption energy reduced gradually with greater electric intensity, and the changing curve of adsorption energy could be fitted as an exponential function, verified by the experiment. The results of this study confirmed the external electric field would be a good strategy for decreasing formaldehyde within building materials in the microcosmic view.

1. Introduction

Formaldehyde as the main volatile organic compounds (VOCs) emitted from building materials are considered to be a major cause of poor indoor air quality [1]. Poor indoor air quality can cause a variety of symptoms such as dry coughs; difficulty concentrating; tiredness; headaches; nose, eye or throat irritations; and dizziness and nausea [2–5]. Therefore, the study of mechanism of formaldehyde adsorption within building materials is very important to help reduce formaldehyde content, especially in the microcosmic level.

Most of scholars were focused on macro-scale study of formaldehyde adsorption within building materials and had little research on microscopic mechanism. The structure of building material was very complicated and it couldn't be constructed completely in micro-scale. Cellulose accounts for more than 70% of wood fiber [6,7] and was the best choice. Cellulose crystals existing in nature are mainly Iα and Iβ [8]. Cellulose Iα exists in the bacterial cellulose and cellulose Iβ exists in the plant and animal cellulose [9,10]. The disaccharide, β-cellobiose, is commonly found as a fragment of the biopolymer cellulose and has importance as a fundamental unit in wood [11]. What's more, first principle studies of cellulose often use cellobiose as the model since it is the smallest repeat unit of cellulose [11–21]. In that case, the β-cellobiose is a best choice and serves as a good model compound in micro-scale for exploring the adsorption of formaldehyde within building materials (Fig. 1) in macro-scale.

The formaldehyde belongs to oxygenated derivative of hydrocarbon. Adsorption of oxygenated derivative of hydrocarbon and β-cellobiose characteristics were investigated by several groups and many achievements had been obtained [22–29]. Frank [27] et al. used the DFT/ab initio calculations to report a very complete set of data at the B3LYP/6–311++G** level of theory for β-cellobiose. Alexander [28] et al. presented the adsorption of glucose, cellobiose and cellotetraose on model surfaces of crystalline cellulose Iα and Iβ. The adsorption energies were calculated with two standard density functional approximations and five dispersion-containing DFT approaches. Faranak [29] et al. used B3LYP/6–311++G** with dispersion correction (DFT-D) to study local and global minimum energy structures of water (H_2O) or carbon dioxide (CO_2) bonding with a pair of cellobiose molecules. The results indicated that penetration of H_2O or CO_2 between adjacent cellobiose pairs, which would assist steam or supercritical CO_2 (SC-CO_2) explosion of cellulose, is not energetically favored. In this work, DFT was used to study the adsorption of formaldehyde on β-cellobiose.

Recently, the external electric field has been identified as a regular and effective method to modulate the properties of adsorption. For example, the adsorption and dissociation of oxygen on pt(111) in the presence of homogeneous electric fields by Hyman [30], effects of

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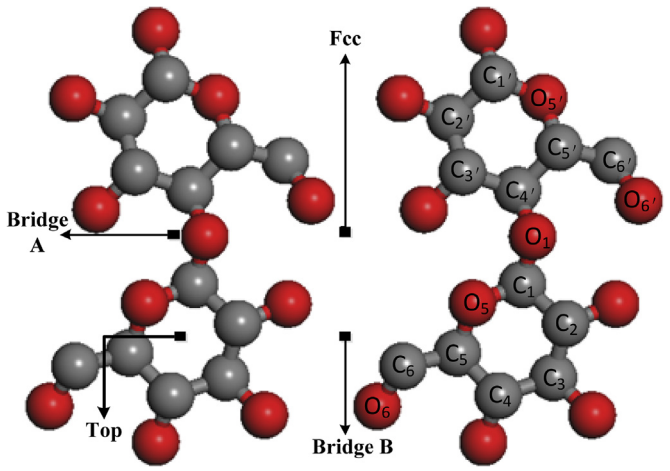

Fig. 1. Top view of the β-cellobiose and adsorbate position (Red - oxygen atom, gray - carbon atom). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

electric potential on hydrogen adsorption by Li [31], adsorption and catalytic activation of O_2 molecule on the surface of Au-doped graphene under an external electric field by Zhang [32], and electric field effects on the adsorption of formaldehyde molecule on the ZnO nanotube surface by Farmanzadeh [33]. What's more, the effect of electric field on formaldehyde adsorption within building materials has been studied by experiment [34]. However, the adsorption of formaldehyde molecule on β-cellobiose under an external electric field in microcosmic view has not been investigated yet. The motivation for this work stems from the need to understand the interaction between formaldehyde molecule and β-cellobiose under an external electric field in micro-scale.

In this study, the adsorption model of formaldehyde molecule on β-cellobiose was built. DFT was applied to study the effect of external electric fields on the geometric structures, molecule bonds and adsorption energy of formaldehyde molecule on β-cellobiose. The simulation results provided a mechanism support for formaldehyde reduction from building materials in microcosmic level.

2. Models and methods

2.1. Models

According to the experimental data from Nishiyama [35], the space group of cellulose Iβ was P21 and the unit cell parameters were as followed: a = 7.784 Å, b = 8.201 Å, c (chain direction and unique axis) = 10.38 Å, $\gamma = 96.5°$.

Two units of β-cellobiose were used for the adsorption of formaldehyde molecule. The structure of the model enables us to capture the major contribution of the top layer to the adsorption, while neglecting the much smaller contributions from lower-lying layers and from neighboring atoms.

In order to obtain the stable structures for adsorption, trial geometries for the optimization were chosen in the following way: formaldehyde molecule regarded as adsorbate was placed at four initial positions including top, bridge A, bridge B and fcc (face-centered cubic), shown in Fig. 1. The four positions contained almost all possible adsorption structures. The adsorbate was first positioned on top of one glucose ring (Top). A second set of trial geometries was obtained by placing the adsorbate between the two glucose rings in one β-cellobiose (Bridge A). Similarly, further trail geometry was obtained by placing the adsorbate between the two glucose rings from two different units of β-cellobiose (Bridge B). The last position was set in the center of four glucose rings (Fcc).

Considering the angle between adsorbate and adsorbent, the adsorbate was positioned parallel and vertical to the adsorbent. Carbon and oxygen atom were set down respectively in the vertical position. All three positions were shown in Fig. 2. Therefore, all twelve trial geometries were built.

3. Methods

The adsorption processes of formaldehyde molecule on β-cellobiose were investigated by DFT. The DFT computations were carried out by DMol [3] code [36] embedded in the Materials Studio software (Accelrys Inc., San Diego, CA, USA). The B3LYP [37–41] density functional combined with a basis set (DNP) including diffuse and polarization terms was used yielding accurate relative energies and structures of hydroxyl-containing compounds like cellobiose [20,42]. The double numerical plus polarization (DNP), which was a higher computational precision being comparable to the Gaussian split-valence basis set 6–31 g**, had been applied in the expanded electronic wave function [43]. In addition, simulation results obtained from the basis set needed to be corrected because of basis set superposition (BSSE) errors for the systems. In addition, all electron core treatment was employed and periodic boundary condition was not used. To ensure high quality results, the self-consistent-field (SCF) density convergence threshold value of 1×10^{-5} Ha (1 Ha = 2625.5 kJ/mol) was specified. A Fermi smearing of 0.05 Ha was applied to improve the calculation performance as well. The convergence criteria included threshold values of 1×10^{-5} Ha, 0.002Ha/Å and 0.005 Å for energy, force, and displacement convergence respectively.

The adsorption energy E_{ads} for formaldehyde adsorption on the β-cellobiose was calculated with the following expression:

$$E_{ads} = E_{\beta-cellobiose} + E_{formaldehyde} - E_{\beta-cellobiose+formaldehyde} \quad (1)$$

where $E_{\beta-cellobiose}$, $E_{formaldehyde}$ and $E_{\beta-cellobiose+formaldehyde}$ stand for the energies of the isolated β-cellobiose, the formaldehyde molecule and formaldehyde-adsorbed β-cellobiose separately.

To investigate the further intensity-dependent behavior, the uniform external electric intensity imposed on the formaldehyde-adsorbed β-cellobiose was varied from 10^{-4} a.u. to 10^{-3} a.u. (1 a.u. = 5.14224×10^{11} V/m) with a step of 10^{-4} a.u. The much higher electric intensity of simulation than that of experiment was used to compensate a short time of simulation. The direction of electric field (EF) was the same as the direction of Z axis in Fig. 2.

3.1. Validations of methods

Selecting a proper simulation method to describe the interactions and adsorption was crucial in this work. As a preliminary test, the atomic structures of the isolated formaldehyde molecule and β-cellobiose were optimized. Using the aforementioned method, the bond length and bond angle of formaldehyde molecule were calculated. The results were as

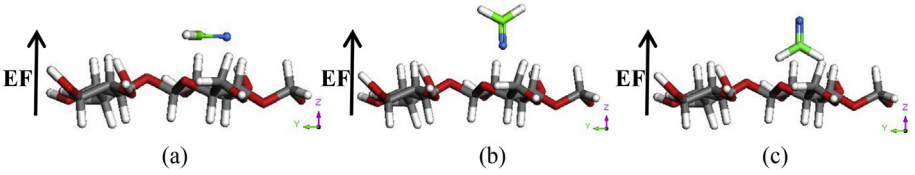

Fig. 2. Side view of adsorbate adsorption angel (a - parallel, b - oxygen atom adown, c - carbon atom adown; White - hydrogen atom, Blue - oxygen atom, green - carbon atom). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)