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A density functional theory study on adsorption and decomposition of acetic acid over silicon carbide nanotubes

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ABSTRACT

In this study, the adsorption behavior of acetic acid (CH_3COOH, AC) over (6,0) zigzag silicon-carbide nanotube (SiCNT) surface are investigated by carrying out density functional theory calculations. The structures of AC-SiCNT complexes are optimized and characterized by frequency calculations at the M06-2X/6-31G* computational level. To understand the catalytic activity of the surface, the interaction between the AC and SiCNT is analyzed by detailed electronic analysis such as adsorption energy (E_{ads}), density of states (DOS), electron density difference and activation barrier. The calculated E_{ads} values are in the range of −0.55 to −3.56 eV. In order to investigate the curvature effect on the adsorption energies of the AC molecule, the AC adsorption on (5,0) and (7,0) SiCNTs is also studied. Our results indicate that the AC adsorption over the narrower (5,0) SiCNT is more thermodynamically favorable process than (6,0) one. So it seems that the curvature of small-diameter SiCNTs facilitates the sp^3-hybridization of Si atoms and thus helps in the binding of AC on the tube surface. For the gas-phase AC decomposition over the SiCNT, the reaction proceeds through an acetate mechanism, which is consistent with the experimental results obtained on metal or metal oxide surfaces.

1. Introduction

The adsorption of carboxylic acids over metal and metal oxide surfaces is of fundamental importance for better understanding their catalytic behavior and adsorption properties. Acetic acid or ethanoic acid (CH_3COOH, AC) is a colorless liquid with a bitter and penetrating odor. It is inflammable and corrosive, having a density of 1.05 g/cm^3 at 20 °C with an auto inflammation temperature of 427 °C [1]. In contrast to formic acid (HCOOH, FM) with 4.4 wt% of hydrogen, AC (7 wt%) can be considered as a desirable hydrogen storage material due to its favorable easy transportation, storage and the possibility of H_2 assertion at room temperature in the presence of metal catalysts [2,3]. According to previous studies [4–11], the AC decomposition process mainly occurs through two reaction channels, namely, decarboxylation and dehydration. Both of these reactions exhibit unimolecular reaction channels involving bond-breaking processes of individual acetate intermediates on the surface. Also, the selectivity of these pathways is related to the special catalyst used. For example, the availability of oxygen from the metal oxide surface is very important for the AC dehydration over metal oxides [12]. Libby et al. [13] suggested that for the dehydration of AC to ketene, the catalyst should have cations with single coordination vacancy in order to facilitate the unimolecular reaction of surface carboxylates. In addition, Martinez et al. [14] indicated that functionalized silica monoliths are highly selective for the production of ketene from AC at temperatures between 650 and 900 K. Later, the same group showed that the AC molecule can be selectively converted to acetone on TiO_2-functionalized monolith catalysts [15]. Interestingly, their results indicated that the formation of acetone on the TiO_2 surface is not a sequential reaction going through an intermediate ketene product. Using infrared and X-ray photoelectron spectroscopy, Bent and co-workers [16] provided an experimental evidence for the O—H dissociation reaction of AC over Ge(1 0 0) surface at 310 K. Their DFT calculations also revealed that for the AC decomposition on a single dimer cluster model, this dissociation reaction is significantly favored, both kinetically and thermodynamically, over other potential reaction pathways. However, despite of all the great efforts made, it is difficult to predict the exact mechanism for the AC decomposition over a given catalyst and the nature of surface intermediates is still under debate.

Since the discovery of carbon nanotubes (CNTs) [17], a large number of theoretical and experimental studies have been devoted to investigate the electronic and structural properties of these new materials [18–21]. CNTs have been attracted much interest due to

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their outstanding properties, like their high surface-to-volume ratios and unique thermal and electronic properties [22,23]. According to earlier studies, doping of CNTs with different atoms such as Si, B and N can increase the surface reactivity of these nanostructures toward the gas adsorption [24–28]. In comparison with CNTs, silicon-carbide nanotubes (SiCNTs), which were first synthesized in 2001 [29], show semiconductor properties regardless of their chirality or diameter [30,31]. Also, due to the intrinsic polarity of Si-C bonds, SiCNTs have a better surface reactivity than CNTs [32–34]. Theoretical calculations show that unlike CNTs, SiCNTs can chemically adsorb molecules such as H_2 [35], CO and HCN [36] with larger adsorption energies. For instance, Kang et al. [37] found that NO and N_2O molecules can be chemisorbed on SiCNTs, while this is not the case for CNTs. Additionally, Wu et al. [38] studied the interaction between two toxic gases (CO and HCN) on SiCNTs and found that SiCNTs exhibit better reactivity toward these two adsorbates than CNTs. Recently, Gao et al. [39] reported a detailed DFT study on the adsorption of a glycine molecule over various zigzag (n, 0) (n = 7, 8, 9 and 10) SiCNTs. Their results indicated that unlike the weak interaction on CNT, the glycine molecule tends to be chemisorbed onto the SiCNTs and the calculated adsorption energy decreases gradually with increased tube diameter because of the curvature effect. On the other hand, our recent studies demonstrated that the SiCNTs can act as an effectively catalyst for the cleavage of the N—H bonds in ammonia–borane [40] and C—H bonds in formamide [41]. Thus, according to these results, SiCNTs can be potentially used as chemical gas sensors for the adsorption of gaseous pollutants as well as metal-free catalysts for decomposition of organic/inorganic molecules.

Here, we employ DFT calculations to investigate the adsorption and decomposition of AC molecule over (6,0) zigzag SiCNT surface. Also, in order to find out the curvature effects on the adsorption properties, the AC molecule adsorption on the (5,0) and (7,0) zigzag SiCNTs is studied. These calculations are performed in order to answer these questions: can SiCNTs be used as a metal-free catalyst for the adsorption and decomposition of AC? If so, what are the possible reaction pathways and intermediates? Upon the adsorption and decomposition of AC with different configurations, the adsorption energy and the activation energy of each reaction step are explained, respectively, and the corresponding mechanisms are analyzed via understanding the electronic structures. As far as we know, this is the first study about the adsorption of AC over the SiCNTs, so, these results could be helpful for developing metal-free catalysts based on SiCNTs.

2. Computational details

All calculations were carried out using DFT framework as implemented in Gaussian 09 [42]. The structures of monomers and complexes were fully optimized and characterized by frequency computations at the M06-2X/6-31G* computational level. M06-2X is a global-hybrid *meta*-GGA functional, with 54% Hartree-Fock exchange [43,44], which has been specifically designed to treat medium-range correlation energy, main group thermochemistry, non-covalent interactions and reaction barriers [45–47]. The (5,0), (6,0) and (7,0) zigzag single-walled SiCNTs with the chemical formula of $Si_{20}C_{20}$, $Si_{24}C_{24}$ and $Si_{28}C_{28}$, respectively, were chosen as the basic models for calculations. The periodic boundary condition (PBC) was used, with a cuboid cell of dimensions $40 \times 40 \times 10.70$ Å. It is noteworthy that the reliability of PBC calculations employed here and the size of the model considered for studying the electronic structure properties of the SiCNTs were validated by results from previous study [48–50]. The adsorption energy (E_{ads}) of the AC on the SiCNT surface is calculated as follows:

$$E_{ads} = E_{AC\text{-}SiCNT} - E_{AC} - E_{SiCNT} \quad (1)$$

where $E_{AC\text{-}SiCNT}$, E_{AC} and E_{SiCNT} are the total energy of the AC-SiCNT complex, the AC, and the pristine SiCNT in the gas phase, respectively. Natural population analysis (NBO) was performed by the NBO 3.1 [51] module in Gaussian 09 at the M06-2X/6-31G* level.

3. Results and discussion

3.1. Adsorption of AC on the (6,0) SiCNT

To study the adsorption properties of AC on the (6,0) SiCNT, the atomic structure of the SiCNT is first examined. Fig. 1 shows the optimized structure of the (6,0) SiCNT. As evident, there are two nonequivalent Si-C bonds in the geometric structure of the SiCNT: one has the bond length of 1.84 Å which is in parallel with the tube axis (named A bond), and another with the bond length of 1.77 Å, in a zigzag form with the tube axis (named Z bond). These bonds lengths are generally in good agreement with previous theoretical reports on the SiCNTs [39–41,52]. The electron localization function (ELF) illustrated in Fig. 1 clearly indicates that the electron-deficient regions of the SiCNT are associated with the Si atoms, while a sizable electron density is localized on the C atoms. Consistent with this picture, NBO analysis indicates a net charge transfer of about 1.9 e from Si atoms to their nearest carbon atoms. As a result, the positive Si atoms and negative C atoms of the SiCNT can be viewed as a Lewis acid and base, respectively.

In order to find the most favorable adsorption configurations, a single AC molecule is placed in several positions above the SiCNT surface with different orientations. After full geometry optimization, four stable configurations are obtained (**A**,**B**, **C** and **D**). These optimized structures and their corresponding binding distances are given in Fig. 2. The calculated binding distance (R), adsorption energy (E_{ads}), Gibbs free energy change (ΔG_{298}), enthalpy changes

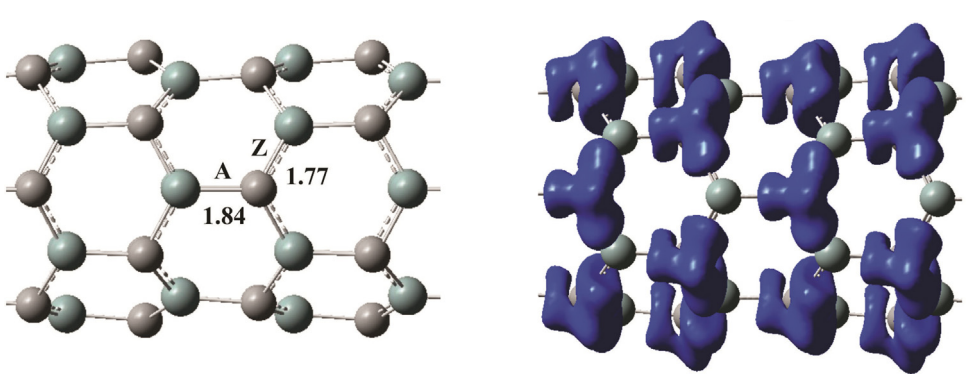

Fig. 1. Geometric structure and ELF isosurface (0.75 au) of the (6,0) SiCNT. All distances are in Å.