Applied Surface Science 290 (2014) 425–432

Contents lists available at ScienceDirect

Applied Surface Science

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

Structure of benzenethiol monolayer on Pt(1 0 0)

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ARTICLE INFO

Article history:
Received 13 September 2013
Received in revised form
17 November 2013
Accepted 18 November 2013
Available online 25 November 2013

PACS:
63.20.dk
81.16.Dn

Keywords:
Molecular self-assembly
Benzenethiol monolayer
First-principle theory
CASTEP
Pt(1 0 0) surface

ABSTRACT

The first-principle technique has been employed to determine the structure of benzenethiol (BT) molecule, molecular chains, monolayers and the BT/Pt(1 0 0) system. Their potential structures have been proposed. CASTEP calculation shows that molecular chains and monolayer are self-assembly system. At the coverage of 0.50 ML, the stable structure in BT monolayer almost stands upright on Pt(1 0 0) in the hollow site, which is in good agreement with the experiment. At the coverage of 0.33 ML and 0.25 ML, when BT monolayer adsorbed on Pt(1 0 0) three adsorption sites are all stable, and the best one is bridge site. The interaction between S atom and Pt surface is stronger than that between BT molecules in the adsorption system.

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1. Introduction

Molecular self-assembly is the spontaneous organization of molecules under thermodynamic equilibrium conditions into well-defined arrangements via cooperative effects between chemical bonds and weak noncovalent interactions [1]. Molecules undergo self-association without external instruction to form hierarchical structures. Molecular self-assembly is ubiquitous in nature and has recently emerged as a new strategy in chemical biosynthesis, polymer science and engineering [2–4].

Because of the particularities of benzenethiol (BT) molecule, the interaction of BT with solid surfaces has attracted much interest in the investigation of the surface adsorption and surface photochemistry, such as Au(1 0 0) [5], Au(1 1 0) [6], Au(1 1 1) [7,8], Cu(1 0 0) [9], Cu(1 1 0) [10], Cu(1 1 1) [11], Ni(1 0 0) [12], Ni(1 1 0) [13], Ni(1 1 1) [14], Pt(1 0 0) [5], Pt(1 1 1) [15], Ag(1 0 0) [16], Ag(1 1 0) [16], Ru(0 0 1) [17] and Rh(1 1 1) [18]. The adsorption structures and reactions when BT molecules adsorbed on the metal surface are the key points. The theoretical calculation of BT on the metal surfaces are exiguous, the first-principle theory [19–21] are used to investigate the structure of BT/Au(1 1 1) system.

The structure of BT molecules on Pt(1 0 0)-($\sqrt{2} \times \sqrt{2}$)$R45^\circ$ with the coverage is 0.50 ML has been proposed by Liu et al. [5] using electrochemical scanning tunneling microscopy (STM). They suggested that BT molecules interacted with Pt(1 0 0) mainly via the sulfur headgroups, whereas the repulsive interaction between phenyl end groups. They observed BT molecules standing upright in the hollow site, but did not investigate the structural parameters. It is clear that STM alone is difficult to determine the alignment of the phenyl groups of BT admolecules. It is difficult to determine the orientation of benzene ring with respect to the surface plane conclusively.

In this paper, the first-principles calculation is intended to reveal the molecular orientation and ordered structure of BT adsorbed on Pt(1 0 0), including the orientation of the benzene ring, the length of Pt—S bond, the adsorption site, the distance between the neighbor BT molecules, the interaction between the neighbor phenyl groups, and the interaction between BT and Pt(1 0 0) surface.

2. Calculation details

2.1. Theoretical methods

Electronic structure calculations are based on density functional theory, and exchange-correlation functional is the most popular Perdew–Burke–Ernzerhof (PBE) generalized gradient

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http://dx.doi.org/10.1016/j.apsusc.2013.11.098

Table 1
The *k*-point meshes, parameters and coverage of BT monomer, Pt crystal, Pt(1 0 0) surfaces, molecular chains, monolayers and BT/Pt(1 0 0) system.

Models	*k*-point meshes	Parameters (nm)	Coverage (ML)
BT monomer	1 × 1 × 1	1.500 × 1.000 × 1.600	–
Pt crystal	4 × 4 × 4	0.400 × 0.400 × 0.400	–
S1	4 × 4 × 1	0.400 × 0.400 × 1.600	0.50
S2	2 × 4 × 1	0.632 × 0.400 × 2.400	0.33
S3	2 × 4 × 1	0.800 × 0.400 × 2.400	0.25
C1	1 × 5 × 1	1.500 × 0.280 × 1.600	–
	1 × 2 × 1	1.500 × 1.000 × 1.600	
C2	2 × 1 × 1	0.713 × 1.000 × 1.600	–
	1 × 1 × 1	1.433 × 1.000 × 1.600	
C3	1 × 4 × 1	1.500 × 0.400 × 1.600	–
M1	4 × 4 × 1	0.400 × 0.400 × 1.600	0.50
M2	2 × 4 × 1	0.632 × 0.400 × 1.600	0.33
M3	2 × 4 × 1	0.800 × 0.400 × 1.600	0.25
M1 on S1	4 × 4 × 1	0.400 × 0.400 × 2.400	0.50
M2 on S2	2 × 4 × 1	0.632 × 0.400 × 2.400	0.33
M3 on S3	2 × 4 × 1	0.800 × 0.400 × 2.400	0.25

approximation (GGA) [22]. Moreover, interactions between core electrons and valence electrons can be described by ultrasoft pseudopotentials.

The tested planewave cutoff energy of 280 eV, which obtains satisfactory results, is used to avoid costly calculations. The convergence criteria for the energy minimization are chosen as below: All Hellmann–Feynman forces are smaller than 0.003 eV/nm, and the energies and displacements are converged to 0.00001 eV/atom and 0.00001 nm, respectively. The Brillouin zone integration is performed on a suitable *k*-point mesh to keep the energy converged. The *k*-point meshes and corresponding parameters of BT monomer, Pt crystal, Pt(1 0 0) surfaces, molecular chains, monolayers and the adsorption system are listed in Table 1. All results are calculated using CASTEP codes [23–26] implemented in the Materials Studio environment [27].

When BT molecule is adsorbed on Pt(1 0 0), the chemisorption energy ΔE_{chem} is defined as:

$$\Delta E_{\mathrm{chem}} = E_{\mathrm{BT/Pt(100)}} - E_{\mathrm{Pt(100)}} - E_{\mathrm{BTmonomer}}$$

where $E_{\mathrm{BT/Pt(100)}}$ is the energy of BT/Pt(1 0 0) system, and $E_{\mathrm{Pt(100)}}$ and $E_{\mathrm{BT\ monomer}}$ are the energies of Pt(1 0 0) and BT monomer, respectively. Energy $\Delta E_{\mathrm{chem}} < 0$ usually means the adsorption system is stable.

When BT molecules stack into the cluster, such as molecular chain and monolayer, the binding energy ΔE_b is defined as:

$$\Delta E_b = E_{\mathrm{BTmonomer}} - E_{\mathrm{BTcluster}}$$

where $E_{\mathrm{BT\ cluster}}$ is the energy of every molecule in BT cluster. Energy $\Delta E_b > 0$ usually means the cluster is stable, the interactions between the neighbor molecules are attractive and it is a molecular self-assembly system.

The literature [9] shows BT monolayer on Cu(1 0 0) is a self-assembly system. If BT molecules assemble the monolayer when BT molecules adsorbed on Pt(1 0 0). Thus, the chemisorption energy $\Delta E'_{\mathrm{chem}}$ should be defined as:

$$\Delta E'_{\mathrm{chem}} = E_{\mathrm{BT/Pt(100)}} - E_{\mathrm{Pt(100)}} - E_{\mathrm{BT\ monolayer}}$$

Then

$$\Delta E_{\mathrm{chem}} - \Delta E'_{\mathrm{chem}} = E_{\mathrm{BT\ monolayer}} - E_{\mathrm{BT\ monomer}} = -\Delta E_b < 0$$

Energy $\Delta E'_{\mathrm{chem}}$ is clearly bigger than ΔE_{chem}. In this case, energy $\Delta E_{\mathrm{chem}} < 0$ does not indicate that the adsorption system is stable enough, only energy $\Delta E'_{\mathrm{chem}} < 0$ means the structure is stable. Hence, in molecular self-assembly adsorption system, the molecular monolayer, not the molecule monomer, should be considered.

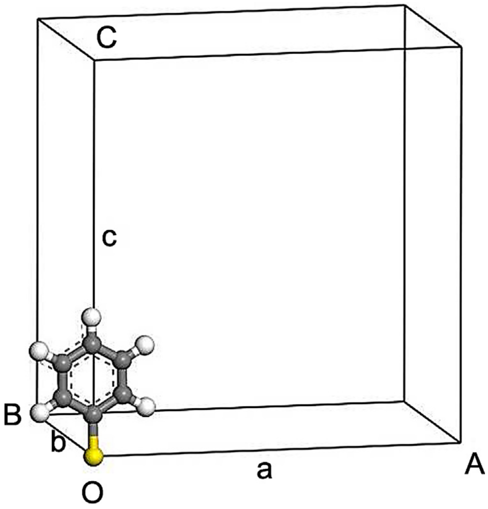

Fig. 1. Original cell of potential structure of BT monolayer, the S atom is set in the vertex of the unit cell.

2.2. Modeling

In our calculations, the potential structure of BT monolayer on the virtual surface is shown in Fig. 1, in which the original cell includes one BT molecule. The S atom is set in the vertex of the unit cell to simulate the virtual S—Pt bond. Three edges, labeled as L_{OA}, L_{OB} and L_{OC}, meet at the origin (O) of the unit cell, their lengths are presented as a, b and c, respectively. The face angles $\angle AOB$, $\angle AOC$ and $\angle BOC$ are all taken as 90°. In order to eliminate the direct tube-tube interaction, the distance (labeled as d) between the nearest atoms of neighbor BT molecules is bigger than 1.000 nm. According to the size of BT planar molecule (0.432 nm and 0.562 nm) three edges of the cell are taken as $a = 1.500$ nm, $b = 1.000$ nm and $c = 1.600$ nm, respectively, to simulate BT monomer. The energy of BT monomer is −1285.758 eV after the geometry optimization.

The optimized lattice constant of Pt crystal increases from 0.392 nm to 0.400 nm. Pt(1 0 0) is set as four layers, the top view of Pt(1 0 0) and the adsorption sites (labeled as top, bridge and hollow) are shown in Fig. 2. The first and second layers are free, and the third and fourth layers are fixed to simulate the solid. The vacuum thickness is taken as 1.800 nm. Pt(1 0 0)-$(2 \times \sqrt{2})R45^{\circ}$ with the coverage is 0.50 ML is labeled as S1, and Pt(1 0 0)-$(\sqrt{2} \times \sqrt{5})R18^{\circ}$ with the coverage is 0.33 ML is labeled as S2, Pt(1 0 0)-$(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ with the coverage is 0.25 ML is labeled as S3. Here the distances

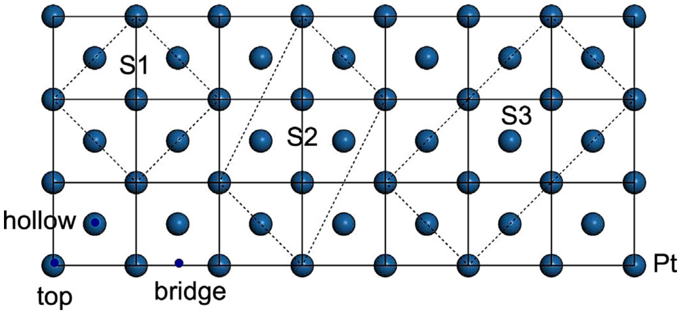

Fig. 2. Sketch map of the structure of Pt(1 0 0), three surfaces (S1–S3) and adsorption sites (top, bridge and hollow) are listed.

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