

Molecular nano-arches on silicon

S. Dobrin

Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, Canada M5S 3H6

Received 30 January 2007; accepted for publication 21 May 2007

Available online 2 June 2007

Abstract

The formation of molecular nano-arches on the Si(111)-7 × 7 surface was modeled using density functional theory (DFT). It has been suggested, based on the calculations, that the arches are formed by molecular dimers of chlorobenzene at near-monolayer coverages. Molecules of the dimer are covalently bound to two silicon adatoms and to each other thereby forming a molecular arch on the surface. The structure of the molecular dimer was calculated at the B3LYP/6-31G(d) level of theory. The dimers were found to be stable at room temperature, and to form a near-monolayer coverage, which has been observed in the experiment [X.H. Chen, Q. Kong, J.C. Polanyi, D. Rogers, S. So, Surf. Sci. 340 (1995) 224; Y. Cao, J.F. Deng, G.Q. Xu, J. Chem. Phys. 112 (2000) 4759].
© 2007 Elsevier B.V. All rights reserved.

Keywords: Chlorobenzene; Silicon surface; Density functional theory (DFT); Molecular nanostructures

1. Introduction

Mechanisms of attachment of organic molecules to the Si(111)-7 × 7 surface attract a lot of attention, because of the potential use of such systems in nano-devices and molecular electronics. In particular, the mechanism of adsorption of chlorobenzene on the Si(111)-7 × 7 surface has been extensively studied recently [1–10]. At low-coverages chlorobenzene chemisorbs on the Si(111)-7 × 7 surface in the form of single molecules by opening a double bond of the aromatic ring and forming two carbon–silicon σ -bonds with a silicon adatom and a restatom [2]. As a result, the molecule is adsorbed in a strained 1,4-cyclohexadiene-like form. This adsorbed structure has a relatively weak adsorption energy (~ 1 eV), due to the molecule losing its aromaticity after attachment to silicon. The structures of adsorbed aromatic molecules have been analyzed theoretically, using semiempirical and DFT calculations [11–15]. Both silicon atoms which are involved in the attachment reaction have dangling bonds, which make

the atoms very reactive, so that the attachment reaction occurs spontaneously at room temperature.

Each unit cell of the Si(111)-7 × 7 surface contains 12 adatoms and six rest atoms. This leads to the saturation of adsorption of single molecules at a coverage of six molecules per unit cell, at which all rest atoms and half the adatoms are occupied [1,2], as shown in Fig. 1a. Half of the adatoms remain unoccupied because the number of adatoms is twice higher than the number of rest atoms. However, an STM experiment shows that at high dosage almost all of the adatoms are covered by chlorobenzene [1]. It is possible to see in the STM images which silicon adatoms are occupied, but it is impossible to distinguish the structure of the adsorbate. Sometimes it is even difficult to distinguish between the adsorbed molecules and defects (missed adatoms), which are always present on the surface in a small amount. However, since the coverage of the defects is much less than a monolayer and does not depend upon the amount of adsorbate, the presence of the defects cannot provide explanation of the STM results obtained at near-monolayer coverages. Neither can the experimental results be explained by chemical reactions or etching of the surface which do not occur at room temperature [1,2]. For these reasons, the high-coverage observed in

E-mail address: sdobrin@chem.utoronto.ca

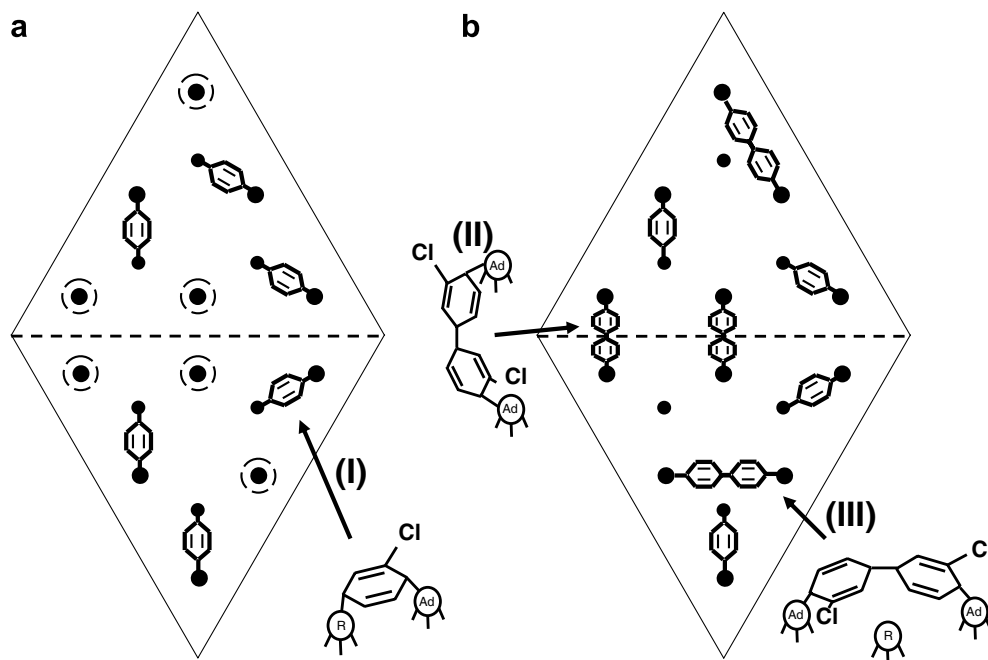


Fig. 1. (a) Saturated coverage, which can be achieved by adsorption of single molecules; (b) higher coverage, which is due to the formation of molecular arches. Adatoms are shown as large circles, rest atoms as small ones. Unoccupied adatoms in (a) are circled. Three different types of adsorption are shown in the schematics: (i) single molecule attached to a silicon adatom and restatom, (ii) an arch over a dimer row, and (iii) an arch over two adatoms of the same half-unit cell.

the experiment must be attributed to molecular adsorption of chlorobenzene, in the form which is different from the low-coverage adsorption. Furthermore, the sticking coefficient of chlorobenzene strongly decreases after half of the adatoms were occupied but does not go to zero, again suggesting that a new mechanism of adsorption takes place at high, near-monolayer, coverages. Such a saturation effect has been also observed in thermal desorption spectroscopy (TDS) and high-resolution electron energy loss spectroscopy (HREELS) experiments [2]. It has therefore been suggested, that a new form of adsorption takes place at high-coverages [1,2], but no explanation of the structure of adsorbates was given. This high-coverage form of adsorption of chlorobenzene on the Si(111)-7×7 surface is the subject of the present work.

2. Results and discussion

On the basis of DFT calculations performed in this study, the high-coverage form of adsorption is attributed to molecular dimers formed on the surface. Two molecules, which form a dimer, are covalently bound to each other by a single C–C σ -bond, and to two silicon adatoms by C–Si σ -bonds, one from each molecule. These arch-like bi(cyclohexa-2,5-dien-1-yl) structures provide a high-coverage of adsorbed chlorobenzene, as shown in Fig. 1b. The arch can be either formed across a dimer row on top of two adatoms of two different unit cells (Type II in Fig. 1b), or on top of two adatoms of the same half-unit cell (Type III in Fig. 1b). The formation of covalently bound molecular

dimers on the Si(111)-7×7 surface has been previously proposed for furan by Cao and co-workers [11] on the basis of their TDS and HREELS experiments combined with PM3 semiempirical calculations. The formation of the dimers was found to be energetically favorable. Furthermore, molecular dimers formed on the Si(111)-7×7 surface due to dispersion forces have been observed recently [16–18].

The DFT calculations reported in this paper have been done for both types of arch-type molecular dimers: molecular arches across a dimer row, and arches on top of two adjacent silicon adatoms of the same half-unit cell. To calculate the structure of the arch adsorbed across a dimer row a 12 silicon-atom cluster, which contains two adatoms (Fig. 2a and b) has been used. To calculate the arch adsorbed on top of two adatoms from the same unit cell, a 14 silicon-atom cluster, which includes two adatoms and one rest atom, has been chosen (Fig. 2c and d). Clusters smaller than these have been successfully used previously to calculate the adsorption and reactions of halogenated benzene on the Si(111)-7×7 surface [6,12]. Similarly to the previous study [12] the 12- and 14-atom clusters used in the present work were first optimized on the AM1 level of theory as parts of large silicon clusters (Fig. 2a and c), having adsorbed molecular dimers. During the AM1 optimization all atoms of the ‘small’ clusters and adsorbed molecules were allowed to relax, while other atoms of the ‘large’ silicon cluster were fixed in their positions. The large cluster used in the AM1 calculations of a dimer row contains the dimer row by itself and six adatoms: three adatoms on the each side of the dimer row. A second large

Download English Version:

<https://daneshyari.com/en/article/5424661>

Download Persian Version:

<https://daneshyari.com/article/5424661>

[Daneshyari.com](https://daneshyari.com)