

Conformation and energetics of benzene adsorbate on SnO₂(110) surfaces: A first principles study

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ABSTRACT

Adsorption of benzene on oxygen rich and reduced SnO₂ surfaces is studied by employing density functional theory calculations, slab model and linear combination of atomic orbitals approach. Rather than preferential adsorption sites, it is found that the adsorption potential energy surface is flat at both surfaces. The bridging oxygen atoms on the stoichiometric surface induce both covalent and ionic bonding leading to weak chemisorptions, whereas bonding on the reduced surface is closer to physisorption. Deformation of the benzene adsorbate due to adsorption is negligible and only small opposite charge transfer is found explaining the differences between the two surfaces.

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1. Introduction

Over the past years, increasing attention has been directed toward the organic functionalization of various semiconductor surfaces due to their potential applications in a number of fields, including molecular electronics, nanoscale lithography, and biosensors [1,2]. Advances in these and other applications can be achieved by combining current knowledge of microelectronics fabrication with the tailorability of organic materials with a precise interface control. Consequently, much effort has been spent to understand and control the interface properties such as molecular orientation [3,4], initial supramolecular organization [5], orbital energy alignment [6,7], tuning the hole or electron injection barrier [7,8], and avoiding the charge-carrier trapping at the interface [9].

Tin dioxide (SnO₂) is a wide band gap (3.6 eV at 300 K) n-type semiconductor. It shows many unique optical and electrical properties: remarkable receptivity variation in gaseous environment, high optical transparency in the visible range (up to 97%), low resistivity (10^{−4} to 10^{−6} Ω·cm^{−1}), and catalytic activity but good chemical stability. These properties make SnO₂ well suited for chemical sensors, transparent conducting electrodes, and various nanodevices [10–13].

During the last years we have carried out a number of studies related to the structure [14,15] and properties [15,16] of tin dioxide surfaces, also including some adsorbates [17,18] and studies of surface chemistry [19,20]. Mainly, the target surface has been the most abundant (110) face in its oxygen rich and poor forms. These two, the

stoichiometric and the reduced surface, are the ideal limiting cases of the intermediate defected ones, which are experimentally observed. These perfect model cases reveal the roles of various type of surface oxygen and lay the basis for understanding the role of more complex oxygen chemistry in surface activity.

Lately, we have focused on understanding the interaction of organic molecules with SnO₂ surfaces. In the present study, we extend our previous work on the adsorption of small hydrocarbon molecules on the SnO₂ (110) surface [20] to aromatic adsorbates and choose benzene as a representative for this class. Benzene has been extensively studied on many surfaces [21–26], but studies on SnO₂ surface remain few. Batzil et al. have studied Benzene on SnO₂(101) surface and found shift of the orbital energies of benzene between stoichiometric and reduced surfaces [27]. To our best knowledge computational studies have not been published, so far.

Based on the comparisons between various adsorbates, we seek broader perspective that enables trends to be observed for the reaction of organic molecules at SnO₂ surfaces to be explained by simple properties of the organic adsorbates such as degree of unsaturation (index of hydrogen deficiency), electron delocalization (local or extended aromaticity), functional groups etc. Such understanding yields predictive power that may provide guidance in designing molecules to achieve specific functionality at the surface. We engage in this work by exploring the deepest level of understanding through *ab initio* electronic structure calculations within the framework of Kohn–Sham density functional theory.

2. Models and methods

Of the different surfaces of tin dioxide, the (110) termination has the lowest surface energy. Therefore, it is the most stable and suitable

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for applications but also for computational analysis [14–18]. We have chosen the two ideal surfaces with this orientation for our study, stoichiometric and reduced ones.

The stoichiometric (110) surface forms in oxygen rich conditions. However, the formation of reduced surfaces is more complex which results in different surface reconstructions with varying amounts of oxygen and defects. Thus, what we have considered in this study can be regarded as a model surfaces the reduced one having high surface energy and being unlikely to form as such. However, these two offer limiting cases that allow assessing the effect and influence of the bridging oxygen atoms to the surface properties of SnO_2 .

Modelling of the surfaces with adsorbates is performed with a supercell that consists of 4×2 surface unit cells to ensure that molecules in neighboring supercells do not interact. 5-layers thick slabs have been used to achieve convergence [20] and the middle layer is constrained to bulk configuration during calculation while the other layers and the molecule are allowed to fully relax. Molecule is introduced on one site of the slab. The dipole interaction caused by this is tested and found negligible (2 meV). The supercell is presented in Fig. 1.

The adsorption energy is calculated as

$$E_{\text{ads}} = (E_{\text{molecule}} + E_{\text{slab}}) - E_{(\text{molecule} + \text{slab})},$$

where $E_{(\text{molecule} + \text{slab})}$ and $E_{\text{molecule}} + E_{\text{slab}}$ are the minimized total energies of the combined adsorbate/ SnO_2 , molecule and substrate systems respectively. E_{molecule} is calculated with the molecule far from the surface, in the middle of the vacuum.

All calculations are carried out using DFT in the linear combination of atomic orbitals (LCAO) approach. There are some advantages in employing LCAO compared to plane-wave (PW) basis. The main advantages lie in the relatively small number of basis functions and unlimited choice of vacuum thickness in between slabs. Furthermore, the LCAO gives a comprehensible description of the molecule–surface interaction in terms of molecular orbitals and substrate bands.

The generalized gradient approximation (GGA) with parametrization by Perdew, Burke and Ernzerhof (PBE) [28] is used with a double numerical basis plus polarization functions (DNP) [29] and an orbital cut-off 4.9 Å. It contains a polarization d function on heavy atoms and a polarization p function on hydrogen. It is comparable in size to the 6-31 G** Gaussian basis set. However, numerical basis sets of a given size are considered to be more accurate than Gaussian basis sets of the same size. Charge distribution analysis is performed with Hirshfeld method [30] that gives basis set independent information about the atomic contributions to charge transfer and redistribution. $2 \times 2 \times 1$ Monkhorst–Pack k-point sampling is used. Thermal smearing of 0.136 eV is used to speed convergence but due to the large band gap the effect on occupation is negligible. Dmol³ software [31,32] which was previously used to successfully study weak interactions in molecular crystals at DFT/PBE level is employed here in all calculations [33].

The basis set superposition error (BSSE) was estimated using the counterpoise method introduced by Boys and Bernardi [34]. This approach uses the same basis functions in the separate system calculations as in the combined system calculation; namely, the separate system energies are calculated by using the full basis set employed in the combined system calculation. This is particularly important for the overly fast decaying tails in Gaussian basis functions but much less important with Dmol³ numerical tails [35]. Nevertheless, in the case of weakly interacting systems, physisorption as opposed to chemisorption at organic-metal oxide interfaces, BSSE can represent a non-negligible fraction of the interaction energy. The BSSE corrected interaction is always less binding than uncorrected.

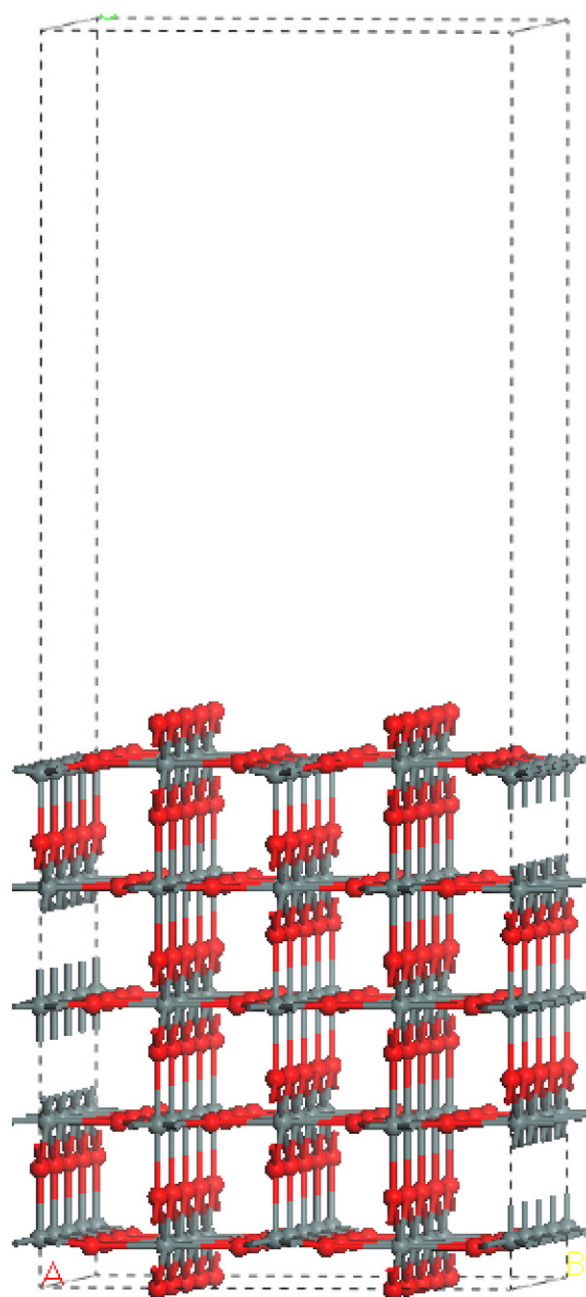


Fig. 1. Slab model of (4×2) stoichiometric surface supercell (size $13.2 \times 13.6 \times 36.3$ Å). Tin atoms are represented in grey and oxygen atoms in red. The reduced surface is formed by removing bridging oxygen atoms. The surface tin atoms form rows of 5-fold and 6-fold (4-fold on the reduced surface) atoms.

3. Results

For both the stoichiometric and reduced surface, several adsorption sites near the high symmetry points of the surfaces were tested. Two sites between the rows of bridging oxygen atoms were chosen on the stoichiometric surfaces. On both sites two orientations for benzene were tested: one where diagonal of the molecule goes parallel to rows of bridging oxygen atoms and another one where the diagonal is perpendicular. Corresponding sites and molecule orientations were tested on the reduced surface and additionally a hollow site between the surface tin atom rows. For every site on both surfaces two calculations were performed: One starting on the high symmetry point and another starting slightly off. Molecule starting distances were 3.3 Å from the

plane of the 5-fold tin atoms on the surface and geometry optimization was performed by energy minimization with force tolerance of 2 mHa/Å. The results corresponding to the highest adsorption energies on each site are presented in Table 1. Adsorption energies in the table are corrected for the basis set superposition error (BSSE).

In most of the present cases, the geometry optimization does not drive benzene far from the initial position. On stoichiometric surface, localization to high symmetry point results in smaller adsorption energy than off-symmetry localization. However, the differences in adsorption energies are small, of the order of 0.01 eV. This implies that the potential energy surface is flat and does not have a clearly localized minimum. Benzene remains flat on the surface, but there is one exception: benzene on the bridge site with its diagonal perpendicular to the row of bridging oxygen atoms. When set in this position benzene not only tilts but also moves away from the high symmetry position and produces adsorption energy that is 0.07 eV larger than off-symmetry localization on the same site.

On the reduced surface, bridge sites produce higher adsorption energies at high symmetry point, but differences are again in order of 0.01 eV. On the top and hollow sites adsorption energies of symmetric and off-symmetric sites are essentially the same. Benzene remains flat on top and bridge sites but tilts on the hollow site. Adsorption energies for all sites on the reduced surface are small and significantly lower than the energies of the corresponding sites on the stoichiometric surface. The effect is weak and might not be fully described with DFT. The description could be improved by more sophisticated methods such as inclusion of van der Waals effect. However, adsorption energy is non-negligible indicating adsorption to the surface.

Adsorbed benzene does not deform, all changes in the molecular geometry are negligible. However, some minor relaxation is observed on the stoichiometric surface. The 5-fold tin atoms and the bridging oxygen atoms nearest to the benzene move slightly towards it (~ 0.05 Å).

Adsorption energies on the stoichiometric surface are higher than on the reduced surface, as indicated in Table 1. Correlated with the fact that adsorption distances are also higher on the reduced surface we conclude that adsorption is stronger on the stoichiometric surface. Comparing the adsorption energies on the same surface it seems that benzene slightly favors the bridging site. However, differences in energies are small. Adsorption sites and energies correlate well with

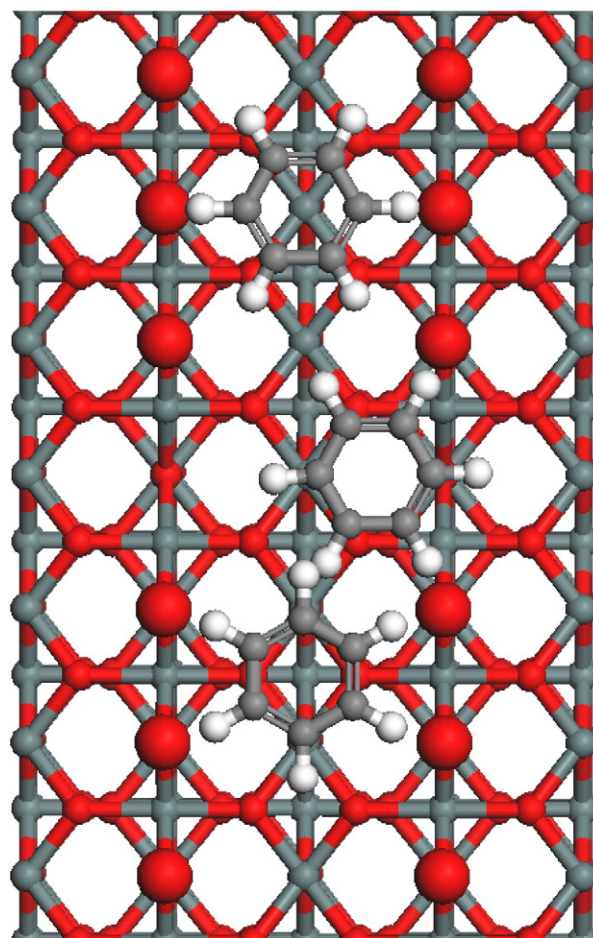


Fig. 2. Possible adsorption sites considered for benzene. Bridging oxygens of the stoichiometric surface are shown with exaggerated balls. From top to bottom the sites are named top, hollow and bridge site. This naming is followed through the article. Top site is situated on top of surface 5-fold tin atom and bridge site is between two such tin atoms. Top and bridge adsorption sites are found on both stoichiometric and reduced surfaces, hollow site on the reduced, only. The two orientations demonstrated for benzene are tested on every site.

Table 1

The BSSE-corrected adsorption energies (E_A) and geometries of the adsorption sites described in Fig. 2. The correction is given in a separate column. Energies for the two orientations of the molecule are presented and where they are the same, only a single value is given. Height is the distance from the plane of 5-fold tin atoms on the surface to the center of benzene. Tilt is the angle of the surface plane and molecule plane measured in the direction perpendicular to the bridging oxygen atom rows. Along the rows atoms benzene lies nearly flat. Adsorption site means distance of the center of the molecule from the high symmetry point of the surface.

	E_A /eV	BSSE/eV	Height/Å	Tilt angle/°	Ads. site/Å
Stoichiometric					
5-fold bridge	0.62/0.68	-0.19	3.3/3.8	0.3/12.3	0.1/0.4
5-fold top	0.45	-0.12	3.7	2.0/0.6	0.2
Reduced					
5-fold bridge	0.11/0.10	-0.14	3.7	0.9/2.0	0.0
5-fold top	0.11	-0.09	4.1	2.2/3.5	0.3/0.2
Hollow	0.09/0.08	-0.10	4.1/4.0	9.9/12.5	0.4

Table 2

Changes in Hirshfeld charges of adsorbed benzene and SnO₂ surface compared to the free molecule and surface (the unit is positive elementary charge).

	Molecule	C	H	Sn 5f	Sn 6f	Oip	Ob
Stoichiometric							
5-fold bridge	0.07/0.19	0.05/0.15	0.02/0.04	-0.07/-0.10	0.03/0.02	-0.02/-0.03	0.03/-0.01
5-fold top	0.06/0.05	0.03/0.03	0.03/0.02	-0.03/-0.02	0.02/0.02	0.00/0.00	-0.01/0.01
Reduced					Sn 4f		
5-fold bridge	-0.03/-0.03	-0.01/-0.02	-0.02/-0.01	0.00/0.00	0.04/0.03	0.01/0.01	-
5-fold top	-0.04/-0.07	-0.03/-0.04	-0.01/-0.03	0.01/0.02	0.03/0.03	0.01/0.02	-
Hollow	-0.02/-0.02	-0.02/-0.02	0.00/0.00	0.01/0.00	0.04/0.04	0.01/0.01	-

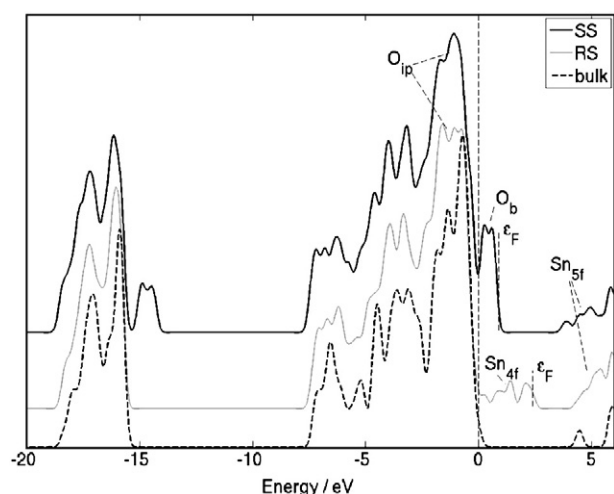


Fig. 3. Density of states (DOS) of bulk tin dioxide (dashed curve), stoichiometric (SS, solid curve) and reduced surfaces (RS, grey curve). Energy scales are matched by positioning the deep states in the figure on top of each other. Thus Fermi energies (ϵ_F) differ and that of bulk is chosen as zero. Contribution of surface atoms on states close to b and gap is marked: in-plane oxygen atoms O_{ip} , bridging oxygens O_b , 4- and 5-fold tin atoms Sn_{4f} , Sn_{5f} .

previously reported data on benzene adsorption on $TiO_2(110)$ surface. Sushko et al. report adsorption energy of 0.38 eV on the top site with cluster Hartree-Fock calculation [36]. Zhou et al. report adsorption energies of 0.67 eV on the bridge site and 0.54 eV on the top site with LDA calculation [37].

Hirshfeld population analysis [30] for the adsorbates is presented in Table 2. There is some charge transfer between the molecule and

the surface though generally relatively small amount of charge (0.02–0.07 electron charges) is transferred. Charge transfer between carbon atoms and the surface 5-fold tin atoms is the strongest effect on all the sites on the stoichiometric surface. One orientation on the bridge site has stronger charge transfer than the rest. This can be related to orientation of the molecule. Benzene tilts strongly bringing one side of the benzene close to surface tin atoms.

Another point of interest is the different behavior of charge transfer on reduced and stoichiometric surfaces. On the stoichiometric surface benzene becomes positively charged and adsorption energy becomes large, on the reduced surface molecule becomes negatively charged and adsorption is weak. This is due to the dangling bond charges of the reduced surface charging the adsorbed molecule. The dangling bond charge is seen in comparing the stoichiometric surface to the reduced one, which has significantly more negative charge on tin atoms (0.24 e on 4-fold and 0.1 e on 5-fold atoms).

Fig. 3 shows the density of states (DOS) of tin dioxide bulk and surfaces. A scissor operator of 2.0 eV is used, which is needed to match the bulk calculated and experimental band gap. Most of the contribution in DOS comes from the bulk states, but bridging oxygen atoms on stoichiometric surface and 4-fold tin atoms on the reduced contribute notably to states above the bulk valence band. It should be noted that the relative weight of the surface contribution depends on the slab thickness of the model. Furthermore, in experimental conditions the surface states are occupied up to the bulk Fermi energy, only. This may effect on the dangling bond charge clearly seen in Fig. 3.

Density of states (DOS) of benzene adsorbed to the surfaces is presented in Fig. 4. Only the bridge adsorption sites are presented as the basic behavior is similar for all the sites. The figure shows downshift of energy levels for both molecules in adsorption. Benzene HOMO level couples with HOMO state of the stoichiometric surface as can be seen by strong broadening which appears in the DOS curve of

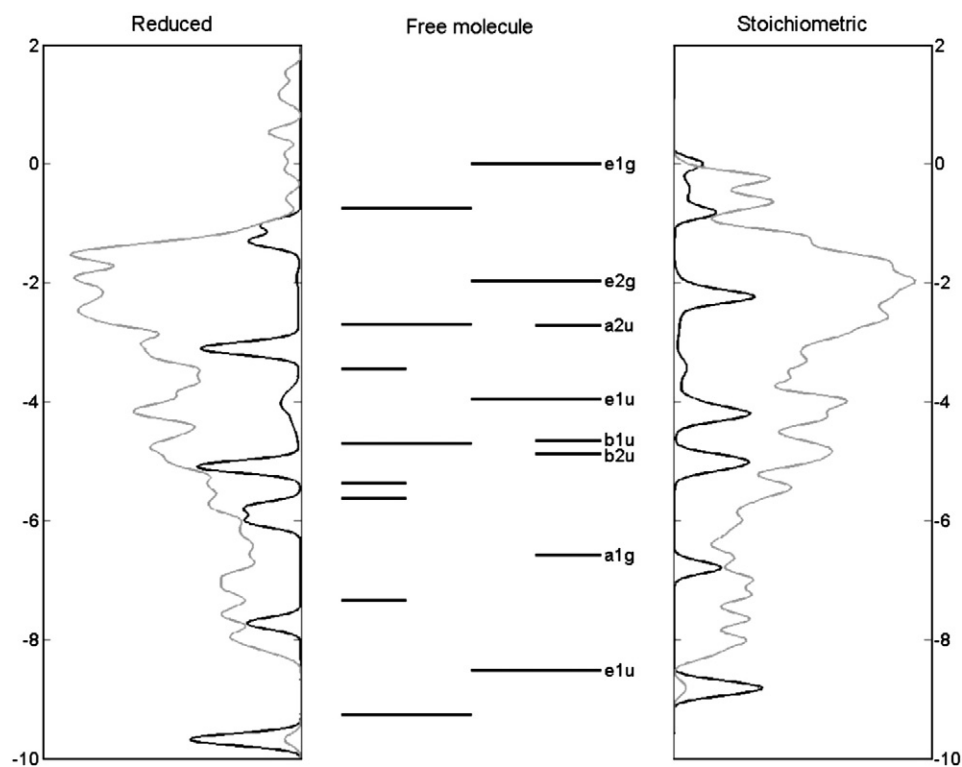


Fig. 4. Density of states (DOS) of adsorbed benzene at bridge sites. Black curves show partial DOS of benzene adsorbed to the surface. Grey curves show total DOS of the surface with adsorbate. The lines in the middle column represent orbital energies, with symmetry species labeled, of free molecule calculated in the vacuum space between two slabs. Energy scales are set by matching deep states of the surface slab. The zero reference is VBM of stoichiometric surface. DOS curves of benzene are scaled up by factor of 5.7 for visibility.

the adsorbed molecule. This implies that adsorption of benzene on the stoichiometric surface includes covalent bonding and interaction with bridging oxygen atoms. On the reduced surface, where bridging oxygen atoms are not available, such broadening is not seen. The adsorption of benzene resembles that of small unsaturated hydrocarbons, whose HOMO state broadens and shifts strongly on the stoichiometric surface and somewhat more weakly on the reduced [20].

4. Conclusions

Benzene adsorption on two SnO₂(110) surfaces was studied. The bridge adsorption site between two 5-fold tin atoms is found to be preferential but only by a small difference in adsorption energy. Two bonding mechanisms are identified on the stoichiometric surface. Broadening of benzene HOMO level suggests covalent bonding and charge transfer between adsorbate and surface tin atoms implies partial ionic bonding. However, adsorption remains weak as adsorption energy is only of the order of 0.7 eV for the strongest site. The adsorption is even weaker on the reduced surface which is evidenced by significantly smaller adsorption energies and higher adsorption height from the surface. This is explained by lack of bridging oxygen atom orbitals that couple with benzene HOMO level on the stoichiometric surface. Additionally, greater negative charge on the reduced surface does not allow charge transfer from benzene to surface, but in fact turns it opposite. Thus, we can conclude that while on the reduced surface adsorption of benzene appears to involve only physisorption, on the stoichiometric surface bonding has also a partial covalent and ionic character.

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