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Full Length Article

Adsorption of carbon monoxide on the Si(111)-7 × 7 surface

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ABSTRACT

The adsorption of CO and surface chemistry of Si are well-understood topics in surface science. However, research into the adsorption of CO on the Si(111)-7 × 7 surface is deficient. In this study, the adsorption of CO on Si(111)-7 × 7 is investigated via high-level density functional theory calculations using cluster model. Two adsorption configurations are found to be kinetically and thermodynamically viable: on-top on rest-atoms and back-bond insertion on adatoms, both binding to the surface via C atom. Structural, electronic, and spectroscopic properties of the adsorbates indicate a σ-donating/π-accepting nature of the CO—Si bonds in both configurations. The domination of σ-donation in the on-top configuration results in a net positive charge on the on-top adsorbate, and the opposite situation yields a net negative charge on the back-bond insertion adsorbates. Our study provides a detailed understanding of the previous experimental observations of fundamental surface chemical phenomena, suggesting possible applications of Si surface functionalization using CO.

1. Introduction

Molecular functionalization of semiconductor surfaces has gained large interest in recent years [1]. Creating well-controlled molecule-solid interface may enable numerous applications in various fields that integrate the properties of the molecular systems with those of the solid substrates [2–4]. The surface chemistry of silicon (Si) has been studied extensively due to its importance in technological applications and interesting scientific aspects [5,6]. For example, clean low-index Si surfaces reconstruct into specific patterns upon annealing under vacuum, such as the Si(111)-7 × 7 surface explained by dimer-adatom-stacking fault (DAS) model [7]. On these surfaces, only a small number of different surface sites appear due to such regular reconstruction and exhibit site-specific reactivity upon adsorption. Due to the covalent and local nature of the chemical bonds of semiconductor surfaces, their chemistry can often be efficiently modeled using small clusters [8] that enable accurate high-level theoretical treatments [9].

The adsorption and reaction of carbon monoxide (CO) on solids are often studied as a model system for understanding the fundamental reactivity or catalytic activity of surfaces [10,11]. Therefore, a variety of techniques has been used to study adsorption and desorption of CO on Si surfaces under vacuum. On the Si(100)-2 × 1 surface, details of two different states of CO were identified: an asymmetric σ-donating structure on the down-atom of a Si dimer (end-on, η^1(C)), and a metastable structure in which the carbon (C) atom is symmetrically bridging between two dimer Si atoms (η^2(C)) [12–17]. However, there have been smaller number of studies of CO on the Si(111)-7 × 7 surface; these studies report a low initial sticking probability and molecular desorption with activation energy of ca. 40 kJ/mol [18–22]. A recent scanning tunneling microscopy (STM) study (ref. [23]) identified two different adsorption geometries on Si(111)-7 × 7, similar to those on Si(100): on-top addition (η^1(C)) and back-bond insertion (BB, η^2(C)). BB of CO was also suggested to form via dissociation of carbon dioxide (CO_2) on Si(111)-7 × 7 [24]. However, the adsorption kinetics and chemical nature of CO adsorbed on Si(111)-7 × 7 are still largely unknown.

In this study, we elucidate the adsorption energetics and chemical properties of different configurations of CO adsorbates on the Si(111)-7 × 7 surface by high-level density functional theory (DFT) calculations using cluster models. In addition to adsorption energies and structures of the adsorbates, C—O vibrational frequency, core-level shifts, and charge transfer at the molecule/Si interface are presented. The results show that CO can assume two configurations on Si(111)-7 × 7: on-top on rest-atoms, and a back-bond insertion on adatoms. Both structures are significantly stabile and do not involve an activation barrier for adsorption. These two configurations are expected to be clearly distinguishable through vibrational or core-level spectroscopic techniques. Both on-top and BB structures involve σ-donation and π back-donation. The direction of charge transfer to/from the surface is opposite for the two adsorption structures.

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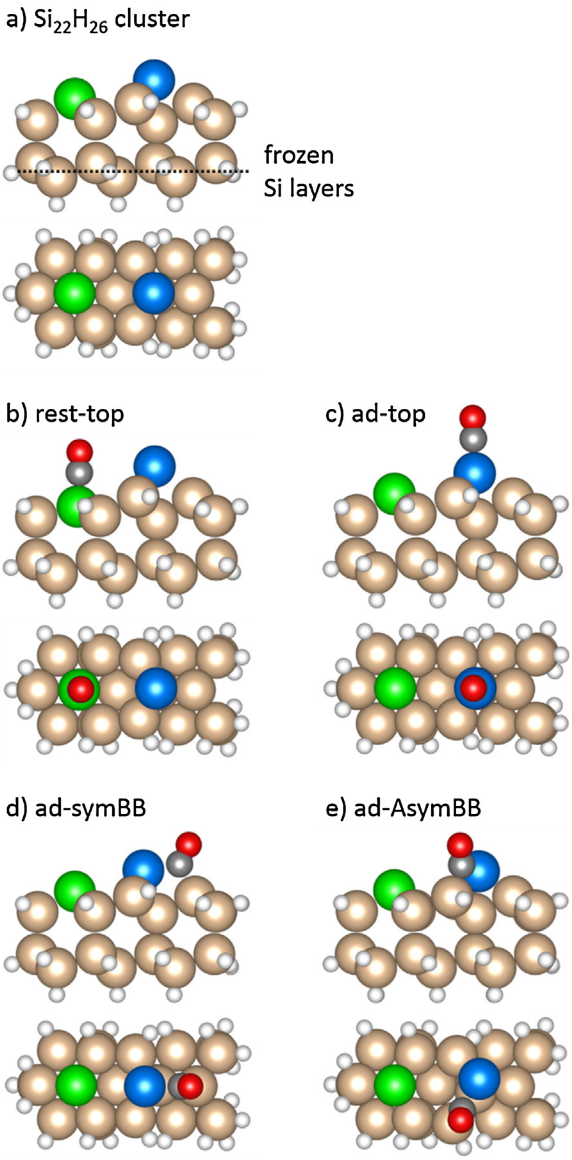

Fig. 1. The geometries of the optimized structures of a) the $Si_{22}H_{26}$ cluster, and b–e) the cluster with CO adsorbates (B3LYP-calculated). Blue = Si adatom, green = Si rest-atom, yellow = subsurface Si, red = O, gray = C, and white = H. PBE0 and M06 geometries are seemingly similar to the B3LYP geometries (not shown). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Bond lengths (r, Å) and orientations against surface plane (a, degrees) of CO adsorbates on Si(111)-7 × 7 (B3LYP-calcualted). r_1 is between C and top layer Si; r_1 is between C and second layer Si. PBE0- and M06-calcualted values are in Table S2, Supporting Information.

	r(C—O)	r_1(C—Si)	r_2(C—Si)	a(CO)
rest-top	1.131	1.884	–	88.9
ad-top	1.132	1.912	–	88.3
ad-symBB	1.191	2.064	2.021	64.5
ad-AsymBB	1.193	2.053	1.976	64.3
TS (ad-top/ad-AsymBB)	1.154	1.838	2.962	43.7
gaseous molecule	1.125			
gaseous molecule (exp., ref. [42])	1.128			

2. Computational details

DFT calculations were performed using ORCA (version 3.0.3) [25]. A $Si_{22}H_{26}$ cluster with four layers of Si and one corner adatom/rest-atom pair (Fig. 1(a)) is used to represent the reactive sites on the Si(111)-7 × 7 surface; a $Si_{21}H_{20}$ cluster with four layers of Si and three dimers is used for the dimer-reconstructed Si(100)-2 × 1 surface. The adsorbates, top two layers of Si atoms, and the terminating hydrogen atoms are relaxed during optimization, while the two bottom layers were fixed at positions of the ideal crystal. Geometry optimizations were carried out using hybrid-GGA B3LYP and PBE0 functionals, and a hybrid-meta-GGA M06 functional, which were some of the best performers for predicting organic molecules' geometries in a recent benchmarking study [26], with a mixed basis set employing def2-TZVP for the adsorbates and top two layers of Si, and def2-SVP for the fixed Si layers and the terminating H atoms. Single point energies of the optimized structures were obtained with dispersion-corrected double-hybrid PWPB95-D3 functional [27] with RI approximation for the MP2 perturbation step [28] and with def2-TZVPPD basis set for the adsorbates and top two layers of Si, and def2-TZVP for the rest of the adduct. RIJCOSX approximation [29] was applied in all calculations for computational speedup. Transition state structures were initially guessed from relaxed potential energy surface scans, and then confirmed after optimization to have an imaginary frequency along the reaction coordinate. Vibrational frequencies were obtained analytically with B3LYP and PBE0, and numerically with M06 using step size of 0.002 bohr (1.06 × 10^{-3} Å). Adsorption energy (E_{ads}) is defined as the difference in electronic energy (E) of [adduct of CO with cluster] with that of [free cluster and free CO] as below:

$$E_{ads} = E(\mathrm{adduct}) - E(\mathrm{cluster}) - E(\mathrm{CO}) \qquad (1)$$

Natural population analysis (NPA) [30] was performed with JANPA (version 1.0.4) [31] after PWPB95-D3 single point calculations to obtain NPA charges and NPA-Wiberg bond orders. Charge transfer from the surface to the adsorbate was defined as the net atomic charge of the adsorbates. Molecular visualization were performed using VESTA (version 3.4.0) [32].

3. Results and discussion

Four different adsorption configurations of CO on Si(111)-7 × 7 were considered (Fig. 1(b–e)): on-top on a rest-atom (rest-top), on-top on an adatom (ad-top), symmetric BB involving an adatom (ad-symBB), and asymmetric BB involving an adatom (ad-AsymBB). It is clear from the geometries that on-top configurations are η^1(C) and BB configurations are η^2(C). Adsorption geometries involving oxygen (O), such as on-top η^1(O), or bridging η^2(C,O) between rest-atom and ad-atom, were also considered, but none of them had stable E_{ads}. In addition, CO adsorbates in the on-top configurations stand nearly upright, i.e., perpendicular to the surface plane, and BB structures are tilted for ca. 25° from the surface normal (Table 1).

Fig. 2 shows the reaction energy diagram of the considered configurations. Only the data from B3LYP optimizations are shown in the main text for simplicity, such as the double-hybrid single point energies in Fig. 2; the values from PBE0- and M06-optimizations are quantitatively similar to the B3LYP ones, and are given in Table S1, Supporting Information. It is noted that adsorption energies from M06 calculations are consistently smaller than the results from other two functionals. Such difference might originate from additional stabilization by dispersion interactions that is provided only by M06, resulting in distortion of the bare $Si_{22}H_{26}$ cluster (Fig. S1, Supporting Information). First, the on-top configurations on rest-atom and adatom can be compared to each other. The formation of both on-top structures involved no activation barrier, as search for the transition states of C—Si bond formation found no saddle point on the potential energy surface above the energy of the reactants. Such results agree with the previous calculations of CO/Si(100)-2 × 1 in which a non-activated adsorption was indicated for the