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Sequential adjacent Si dimer dechlorination mechanism of perchloroethylene adsorption on Si(1 0 0) with temperature evolution

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ABSTRACT

To elucidate the peak shifting of C-1s in X-ray photoelectron spectrum (XPS) of perchloroethylene (PCE) adsorption on Si(1 0 0), the sequential adjacent Si dimer dechlorination mechanism was proposed based on first principles calculations. The highly-symmetric Cl atoms of PCE induce three possible initial di-dechlorination processes occurring on intra, inter-dimer and *iso* intra-dimer, respectively, to yield three tetra-σ states. These tetra-σ states are identified to coexist at room temperature (RT) due to the relatively low reaction barriers (<0.59 eV). However, their further di-dechlorination to form intra and inter-dimer hexa-σ states requires much higher activation barriers (>1.08 eV), which leads to hexa-σ states only exist at elevated temperatures although they are found to be the most stable in terms of energetics. The calculated ionization energies (IEs) of C-1s core electron and vibrational frequencies of various potential adspecies are well consistent with the experimental data observed by XPS and vibrational electron energy loss spectroscopy (EELS), which further corroborates the sequential dechlorination processes of PCE on Si(1 0 0).

1. Introduction

Understanding the molecular adsorption mechanism on silicon surface is of fundamental interest in incorporating various functionalities into Si-based devices [1–6], to realize potential applications of silicon derivatives in semiconductor industry. Halogenated derivatives of the simplest unsaturated hydrocarbons are good candidates to elucidate the basic chemical processes upon their adsorptions on reconstructed Si surface [7–11]. For example, dibromoethylene (DBE), *cis*, *trans* and *iso*-dichloroethylene (DCE, $C_2H_2Cl_2$) were observed to exhibit a common feature that halogen atoms were dissociated from the adsorbates after adsorption on Si(1 0 0) [12–17]. A subsequent first principles study found that adjacent Si dimer di-dechlorination mechanism rather than insertion mechanism was more favorable in dissociating Cl atoms to Si surface, which excellently elucidated the C-1s peak shifting of DCE adsorption on Si(1 0 0) with temperature evolution[12,13].

Recently, to understand the multi-halogen effect on the dechlorination process, X-ray photoelectron spectra (XPS) and temperature-programmed desorption (TPD) mass spectrometry experiments were carried out to extend the study of $C_2H_2Cl_2$/Si(1 0 0) to perchloroethylene (PCE, C_2Cl_4) adsorption on Si(1 0 0) [16]. In their XPS, three C-1s features were observed to be distributed at 283.9, 285.2, and 287.0 eV at room temperature (RT), corresponding to three C environments: C_α ($=C_\alpha<^{Si}_{Si}$), C_β ($=C_\beta<^{Cl}_{Si}$), and C_γ ($=C_\gamma<^{Cl}_{Cl}$), respectively. When the sample was annealed to 800 K, the intensity of the C_α-1s peak at 283.9 eV reached a maximum, while the relative intensity of C_β-1s and C_γ-1s peaks nearly disappeared completely. Compared to the only two-splitting C-1s features exhibited by DCE/Si(1 0 0) [16,17], the three-splitting C-1s peak shifts with temperature evolution implies that PCE may undergo a more complicated dechlorination process on Si(1 0 0). In contrast to the notable splitting levels of 1.3 and 1.8 eV for C_α and C_γ relative to C_β, Cl-2s exhibited broad peaks centered at 270.6 and 270.1 eV in different temperatures.

The adsorption of PCE on Si(1 0 0) is expected to undergo more complicated chemical process with thermal evolution, since PCE is highly symmetric and combines all the features of *cis*, *trans* and *iso*-DCE. Two pivotal issues to be addressed at first are how the four Cl atoms are dissociated from PCE, and how the resulting adspecies at RT convert to the final adspecies at high temperature. To tackle these questions, we first investigated a series of feasible adsorption configurations, which are derived from single, double and quadruple C—Cl bond cleavages, based on previously identified adjacent Si dimer dechlorination mechanism. To help assign the adspecies and their conversions, the core electron ionization energies (IEs) and vibrational frequencies of all the plausible adsorption states were calculated to compare with the C-1s peak shifting in XPS and characteristic stretching variation in vibrational EELS [18]. The adsorption and transformation processes between adspecies were

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explored to evaluate the reaction barriers, which is useful to understand the peak shifting at high temperature.

2. Computational method

The total energy and electronic structure calculations were carried out within density functional theory (DFT) framework in VASP [19–24], with planewave basis set and Vanderbilt ultrasoft pseudopotentials (US-PP) [19,20,25,26]. The PW91 exchange-correlation functional in general gradient approximation (GGA-PW91) [27–30] was applied, since PW91 has been examined to present consistent results with those obtained by PBE and B3LYP exchange correlation functionals in previous study on *iso*-DCE/Si(100) [13]. The cutoff energy was set to be 300 eV for the plane-wave expansion. The slab model containing a (4×2) supercell was chosen to be parallel and perpendicular to Si dimer row, respectively, for calculating intra and inter dimer dechlorination process. The slab contains five Si layers with the top layer containing two $p(2 \times 2)$ units of asymmetric silicon dimers and the bottom Si atoms being saturated by H atoms, with the vacuum space along z axis of 10 Å. A set of Monkhorst Pack $4 \times 4 \times 1$ *k*-points were used to sample the Brillouin zone, which maintains the previous setting in the unit cell $p(2 \times 2)$ of $C_2H_2Cl_2$ adsorption on Si(100) for comparison [12,13]. The calculated electronic energy of this (4×2) supercell was nearly two times than that of (2×2) unit cell, implying that the choice of these *k*-points is reasonable. All atoms except for the bottom Si and H layers were allowed to fully relax. The adsorption energies (E_{ads}) of the proposed adstructures were calculated according to the definition $E_{ads} = E_{PCE/Si(100)} - E_{Si(100)} - E_{PCE}$. The minimum energy reaction pathway was mapped out by using the climbing nudged elastic band (cNEB) with inserting 6–8 images between the given initial and final states [31–33]. All the saddle points along the reaction pathways were verified to be the real transition states by calculating their vibrational frequencies using the dynamic matrix method [34]. Similar to the previous studies, the IE differences of core electrons including C-1s and Cl-2s were obtained based on the Koopmans theorem [35] using the projector augmented wave (PAW) potential [36,37].

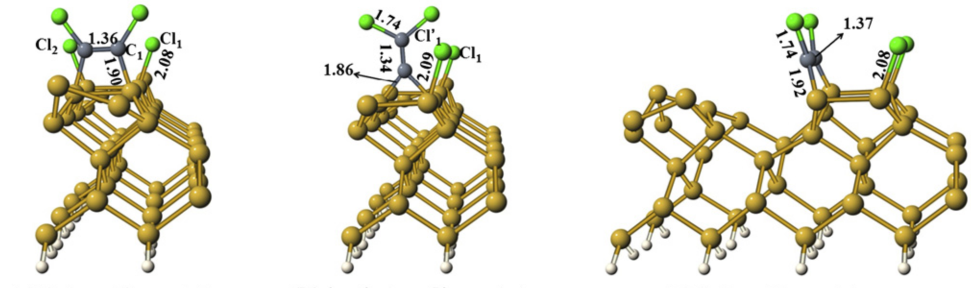
3. Results and discussion

3.1. Potential adspecies

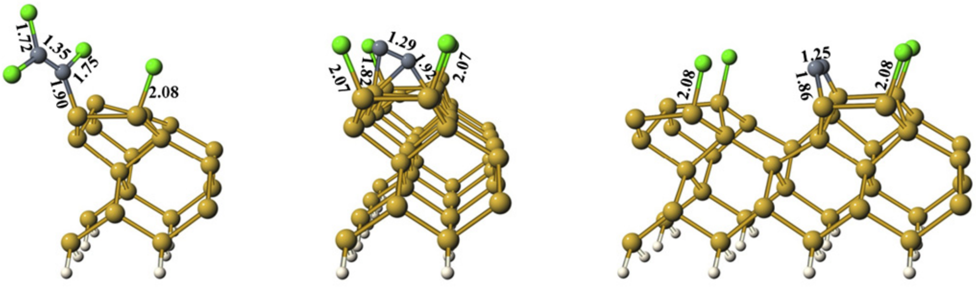
A significant difference of PCE compared to DCE is its total-substitution of H atoms by Cl atoms. Hence, an important factor to reveal the final dechlorination adstructures is to ascertain whether tetra-dechlorination adspecies exist or not. In the light of identified adjacent Si dimer dechlorination adspecies of DCE/Si(100) [12], we studied and optimized six types of potential adstructures, including mono-, tetra- and hexa-σ states, as shown in Fig. 1. Particularly, *iso* intra-dimer di-dechlorination adspecies (Fig. 1b) were taken into account in addition to intra and inter-dimer tetra-σ di-dechlorination structures (Fig. 1a and c). In the newly-proposed *iso*-intra-dimer tetra-σ, the remained $C_2<^{Cl}_{Cl}$ up-stands along $C_1{=}C_2$ bond while C_1 binds intra-dimer Si atoms to form a triangle Si—C—Si bond after dissociating two Cl atoms onto opposite Si dimer. Here, we should emphasize that only *cis*-di-dechlorination adspecies were studied for simplification, owing to the similar dechlorination process exhibited by *cis* and *trans*-DCE adsorption on Si(100) in previous studies [12,13]. A further di-dechlorination from tetra-σ structures will produce intra or inter-dimer hexa-σ states (Fig. 1e and f), in which all the four Cl atoms are dissociated onto opposite Si dimers or vacant Si atoms to form a shorter $C{\equiv}C$ bond (1.29 or 1.25 Å) and six σ bonds including two C—Si and four Cl—Si bonds. The E_{ads} listed in Table 1 presents an obvious trend that it is enlarged with increasing the number of broken C—Cl bonds. As a result, mono-σ state (Fig. 1d) derived from single dechlorination is the least stable structure with the smallest E_{ads} of 2.96 eV, while intra and inter-dimer hexa-σ states derived from quadruple dechlorination are the most stable structures with $E_{ads} = 7.31$ and 7.42 eV, respectively. Next we will address how the four Cl atoms are dissociated onto Si dimers from the kinetic point of view.

3.2. Di-dechlorination process at RT

The XPS experiment has observed three C-1s features of PCE/Si(100) adsorption, which indicated that multiple C—Cl



(a) intra-dimer tetra-σ (b) iso intra-dimer tetra-σ (c) inter-dimer tetra-σ



(d) mono-σ (e) intra-dimer hexa-σ (f) inter-dimer hexa-σ

Fig. 1. The adstructures and geometry parameters of different adspecies of PCE on Si(100), derived from single, double and quadruple dechlorination processes.