



# Selective surface chemistry of allyl alcohol and allyl aldehyde on Si(100)2×1: Competition of [2 + 2] C=C cycloaddition with O–H dissociation and with [2 + 2] C=O cycloaddition in bifunctional molecules

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## ABSTRACT

Competition between the C=C functional group with the OH group in allyl alcohol and with the C=O group in allyl aldehyde in the adsorption and thermal chemistry on Si(100)2×1 has been studied by X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD), as well as density-functional theory (DFT) calculations. The similarities found in the C 1s and O 1s spectra for both molecules indicate that the O–H dissociation product for allyl alcohol and [2 + 2] C=O cycloaddition product for allyl aldehyde are preferred over the corresponding [2 + 2] C=C cycloaddition products. Temperature-dependent XPS and TPD studies further show that thermal evolution of these molecules gives rise to the formation of ethylene, acetylene, and propene on Si(100)2×1, with additional CO evolution only from allyl alcohol. The formation of these desorption products also supports that the [2 + 2] C=C cycloaddition reaction does not occur. In addition, the formation of SiC at 1090 K is observed for both allyl alcohol and allyl aldehyde. We propose plausible surface-mediated reaction pathways for the formation of these thermal evolution products. The present work illustrates the crucial role of the Si(100)2×1 surface in selective reactions of the Si dimers with the O–H group in allyl alcohol and with the C=O group in allyl aldehyde over the C=C functional group common to both molecules.

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## 1. Introduction

Surface chemistry of multifunctional organic molecules on Si(100)2×1 has attracted a lot of attention in the past decade [1–7]. The electrophile–nucleophile character of the buckled silicon dimers [8,9] on the Si(100)2×1 surface provides unique control of how this surface reacts with different functional groups. The buckling of the Si dimers enables the [2 + 2] cycloaddition reaction with alkene at room temperature (RT), which is normally symmetry-forbidden in classical chemistry by the Woodward–Hoffman selection rules [10]. To date, surface reactions of alkenes (with the C=C functional group) [6,11–24], aldehydes [25,26] and ketones (both with the C=O functional group) [25,27,28] on Si(100)2×1 have been reported to form [2 + 2] and [4 + 2] cycloaddition products, while those of alcohols (with the OH functional group) [29–34], carboxylic acids (with the COOH functional group) [35–44], and primary and secondary amines have resulted in H dissociation products [1,5,6]. These studies illustrate the critical role of the silicon surface in mediating selective chemical reactions largely involving a single functional group.

In order to investigate the selectivity of the 2 × 1 surface toward the aforementioned functional groups, we employ a molecule that contains multiple functional groups as the adsorbate, and study its thermal surface chemistry by using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD), along with density-functional theory (DFT) calculations. In our recent work on acrylic acid [44], the simplest unsaturated carboxylic acid containing two functional groups, we compared the reactivity of the carboxyl group and ethenyl group in this bifunctional molecule with those of saturated carboxylic acids: acetic acid [43] and propanoic acid, both containing just the carboxyl group [44]. In particular, we showed that the Si(100)2×1 surface selectively favours O–H dissociation of the carboxyl group over [2 + 2] C=C cycloaddition of the ethenyl group and other possible reaction products in acrylic acid. As was also found for acetic acid [43] and propanoic acid [44], O–H dissociation in acrylic acid also leads to bidentate and unidentate carboxylate adspecies.

Using the ethenyl group as the “reference” functional group, we now extend our study of relative reactivity and selectivity of the carboxyl group [44] to other functional groups in a bifunctional molecule on Si(100)2×1. In particular, allyl alcohol (or 2-propenol, CH<sub>2</sub>=CH–CH<sub>2</sub>OH) and allyl aldehyde (or 2-propenal, CH<sub>2</sub>=CH–CHO) offer the hydroxyl group (OH) and carbonyl group (C=O), respectively, as the second functional group, in addition to the

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common ethenyl group ( $\text{CH}_2=\text{CH}-$ ). In acrylic acid [44] (and carboxylic acids in general), the carboxyl group itself could be considered as consisting of two smaller functional groups, the OH and C=O. The present work, in effect, compares the competition of the ethenyl group with each of these smaller functional groups individually in their reactions with the  $2 \times 1$  surface. To date, no experimental study has been reported for the adsorption of allyl alcohol and allyl aldehyde on  $\text{Si}(100)2 \times 1$ . Only one DFT computational study [using the B3LYP/6–31G(d) method] of allyl alcohol on model  $\text{Si}(100)$  and  $\text{Ge}(100)$  cluster surfaces has been reported by Li et al. [45]. Their calculations showed that O–H dissociation results in more thermodynamically favourable products than  $[2+2]$  C=C cycloaddition products.

In the present work, we present XPS and TPD studies to follow the thermal evolution of the adsorption products of allyl alcohol and allyl aldehyde on  $\text{Si}(100)2 \times 1$ . Together with our DFT calculations, these experimental results show that for allyl alcohol O–H dissociation is preferred over  $[2+2]$  C=C cycloaddition, as was proposed by Li et al. [45] and was also observed for other carboxylic acids [41,44]. For allyl aldehyde,  $[2+2]$  C=O cycloaddition is found to be more favourable than  $[2+2]$  C=C cycloaddition by our XPS measurement, in spite of the less negative calculated adsorption energy obtained for the former product than that for the latter by our DFT calculation. The present work therefore further affirms the remarkable stability of the ethenyl group relative to any of the following functional groups: OH, C=O (this work), COOH [44], and Cl [46,47] as well as other heteroatom-containing groups [6], on the  $2 \times 1$  surface. These latter functional groups (except Cl) can therefore be used as the linkage to connect the molecule to the  $2 \times 1$  surface, leaving the ethenyl group free for further reactions. Furthermore, the present experimental result also shows that multiple linkages through simultaneous interactions of two functional groups with the surface (such as the [O, C, C] tridentate and the [O, C] bidentate adstructures) do not occur, despite the considerably more negative adsorption energy calculated for these multiply bonded adstructures. The formation of ethylene, acetylene, and propene fragments found in our TPD experiments for both allyl alcohol and allyl aldehyde adspecies further supports that the common unreacted moiety (the ethenyl group) remains intact and free to undergo further thermal chemistry upon adsorption on  $\text{Si}(100)2 \times 1$ .

## 2. Experimental and computational details

All of the experiments were performed in a home-built, dual-chamber ultrahigh vacuum system with a base pressure better than  $1 \times 10^{-10}$  Torr. Our experimental setup and procedure have been described in detail elsewhere [48]. Briefly, the sample preparation chamber was equipped with an ion sputtering gun, and a four-grid retarding-field optics for both reverse-view low energy electron diffraction and Auger electron spectroscopy. A  $14 \times 10 \text{ mm}^2$  substrate was cut from a single-side polished, p-type B-doped  $\text{Si}(100)$  wafer (0.4 mm thick) with a resistivity of 0.0080–0.0095  $\Omega \text{ cm}$ . The Si substrate was pre-cleaned in the preparation chamber by cycles of  $\text{Ar}^+$  sputtering (20 mA emission current, 1.5 kV beam energy) for 20 min at RT followed by annealing to 900 K for 5 min. The substrate was then flash-annealed to 1100 K for 20 s to obtain the  $2 \times 1$  reconstructed surface. The cleanliness of the  $2 \times 1$  surface was verified by the sharpness of the electron diffraction pattern and by our XPS data that showed no significant contamination. The clean Si substrate was then exposed to allyl alcohol (99.0% purity) or allyl aldehyde (90.0% purity), both purchased from Sigma–Aldrich, after appropriate thorough degassing of the colorless liquid chemicals by repeated freeze–pump–thaw cycles. All exposures were performed at RT by using a variable leak

valve with the pressure monitored by an uncorrected ionization gauge, and reported in units of Langmuir ( $1 \text{ L} = 10^{-6} \text{ Torr s}$ ). The high purity of the exposed chemical was confirmed by its cracking pattern obtained in situ. Saturation exposures were used for both the TPD and temperature-dependent XPS experiments unless stated otherwise.

TPD mass spectrometry and XPS experiments were conducted in the analysis chamber. For the TPD studies, a differentially pumped 1–300 amu quadrupole mass spectrometer (VG Quadrupole SXP Elite) was used, along with a home-built programmable proportional–integral–differential temperature controller to provide linear temperature ramping at an adjustable heating rate, typically set at  $2.0 \text{ K s}^{-1}$ . A type-K thermocouple (wrapped in a Ta foil) was mechanically placed in good contact with the front face of the sample to measure the temperature. The temperature of desorption maximum for the recombinative desorption of  $\text{H}_2$  was used to calibrate the temperature scale [49]. To ensure that the selected mass fragments originate only from the species desorbed from the Si surface, the sample was positioned within 1 mm to the orifice (2 mm dia.) at the entrance of the differentially pumped housing of the mass spectrometer. Unless stated otherwise, the desorption profiles have been smoothed by adjacent averaging for clarity. For the XPS experiments, an electron spectrometer (VG Scientific CLAM-2), consisting of a hemispherical analyser of 100 mm mean radius and a triple-channeltron detector, was used, along with a twin-anode X-ray source that supplied unmonochromatic Al  $K_\alpha$  radiation (1486.6 eV photon energy). XPS spectra were collected with an acceptance angle of  $\pm 4^\circ$  at normal emission from the silicon sample, and with a constant pass energy of 50 eV, giving an effective energy resolution of 1.4 eV full-width-at-half-maximum for the Si 2p photopeak. The binding energy scale of the XPS spectra has been calibrated to the Si 2p feature of the bulk at 99.3 eV. Spectral peak fitting based on residual minimization with Gaussian–Lorentzian lineshapes was performed by using the CasaXPS software. For temperature-dependent XPS measurements, the sample was flash-annealed to the preselected temperature and cooled back to RT before collecting the XPS spectra.

The DFT [50] method in the Gaussian 03 software package [51] was used to calculate the electronic structures of the adstructures. The hybrid B3LYP functional, composed of Becke's three-parameter gradient-corrected exchange functional [52] and the Lee–Yang–Parr correlation functional [53], was employed. The DFT/B3LYP method has been shown to provide generally good agreement with the experimental data for the adsorption of many molecular systems on  $\text{Si}(100)2 \times 1$  [5]. We performed the present calculations using four basis sets: 6–31G(d), 6–31+G(d), 6–31++G(d) and 6–31++G(d,p), all of which gave similar results for the optimized geometries and total energies (with the larger basis set providing a lower total energy). Frequency calculations were also performed for all of the optimized geometries, in order to ascertain that the local minima correspond to the equilibrium structures and not transition-state structures. In the present work, the  $\text{Si}(100)2 \times 1$  surface was simulated by the double-dimer surface of a  $\text{Si}_{15}\text{H}_{16}$  cluster. The adstructures of allyl alcohol and allyl aldehyde were fully optimized without any geometrical constraint on the  $\text{Si}_{15}\text{H}_{16}$  cluster. The corresponding adsorption energy (for allyl alcohol and allyl aldehyde),  $\Delta E$ , was estimated by the difference between the total energy for an optimized structure of the adsorbate–substrate configurations (ASCs) of the adsorbate on the  $\text{Si}_{15}\text{H}_{16}$  model surface and the sum of the total energies of the free molecule and of the  $\text{Si}_{15}\text{H}_{16}$  cluster. All the total energies were obtained without zero-point correction and no basis set superposition error correction was made to  $\Delta E$ .

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