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Competing Forward and Reversed Chain Reactions in One-Dimensional Molecular Line Growth on the Si(100)−(2 × 1)−H Surface

Md. Zakir Hossain,*,† Hiroyuki S. Kato,† and Maki Kawai*,†,‡

RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan, and Department of Advanced Materials, The University of Tokyo, Kashiwa, Chiba 277-8501, Japan

Received November 3, 2006; E-mail: maki@riken.jp; zakir@riken.jp

Abstract: To explore the role of competing forward and reversed chain reactions in the growth of a one-dimensional (1D) molecular line on the Si(100)−(2 × 1)−H surface, controlled experiments were performed with various alkene molecules by scanning tunneling microscopy (STM) at various temperatures. It was observed that the end dangling bond (DB) of a styrene line, fabricated by a chain reaction on the Si(100)−(2 × 1)−H surface at 300 K, initiated a reverse chain reaction at 400 K, leading to the complete disappearance of the styrene line with zero-order desorption kinetics (rate constant $k = 1.17 \times 10^{-2}$ s^{-1} at 400 K). In the case of 2,4-dimethylstyrene, the reversed chain reaction was observed even at 300 K. These results suggest that the appearance of a molecular line in an STM image is determined by the rates of competing forward and reversed chain reactions at a given temperature. As predicted, 1D lines formed by the DB-initiated chain reaction of 1-hexene and 1-heptene on Si(100)−(2 × 1)−H were observed at 180 K because of the reduced desorption rate, despite the fact that those molecules showed no line growth at 300 K. These results indicate that the scope of forming 1D molecular lines on the Si(100)−(2 × 1)−H surface with various alkenes is much wider than anticipated in previous studies.

Introduction

The unpaired dangling bond (DB)-initiated radical chain reaction of alkene molecules on the Si(100)−(2 × 1)−H surface has emerged as one of the most promising approach to fabricating one-dimensional (1D) molecular line with predefined position, length, composition, and structure.[1−6] The end of a molecular line fabricated by a chain reaction mechanism always has a DB unless terminated by some means (discussed below).[1] A recent observation of the electronic effects of a charged DB on aligned molecular orbitals of a styrene line along the dimer rows on the Si(100)−(2 × 1)−H surface has opened a new possibility of using such molecular lines in future silicon-based molecular devices.[7] In addition to electron transport through a molecular line, molecular line junctions might show the properties of gating, switching, sensing, and transistor functions.[7−9]

In spite of a number of studies involving the formation of a molecular line on the Si(100)−(2 × 1)−H surface through the chain reaction mechanism,[1−6] it is not yet directly determined if an end DB of a growing line can initiate a chain reaction in the reverse direction, leading to the desorption of molecules in a line. In addition to the thermal stability of a molecular line, a reversed chain reaction may also relate to the unexpected observations that only a limited number of alkene molecules undergo a chain reaction to form a 1D molecular line at 300 K.

Some molecules such as styrene ($CH_2{=}CH{-}Ph$),[1,6] vinyl ferrocene,[4] long-chain alkenes (C_nH_{2n}, $n \geq 8$),[5] 2,4-dimethylstyrene, allyl mercaptan ($CH_2{=}CH{-}CH_2{-}SH$)[2,3] undergo a DB-initiated chain reaction on the Si(100)−(2 × 1)−H surface, whereas other alkenes such as propylene ($CH_2{=}CH{-}CH_3$),[1] 1−heptene,[5] vinyl cyclohaxane,[5] 4-vinylpyridine,[3] and allyl methyl sulfide ($CH_2{=}CH{-}CH_2{-}S{-}CH_3$)[2] show no line growth at 300 K. Such a chain reaction involves the interaction of a $>C{=}C<$ site in the alkene molecule with a DB on the Si(100)−(2 × 1)−H surface resulting in the formation of a carbon (C)-centered intermediate radical and then the abstraction of a H atom from an adjacent Si−H site by the intermediate radical.[1,2,10] The abstraction of H creates a new DB site adjacent to the adsorbed molecule, which can react with another alkene molecule. The stabilization of the C-centered radical is believed to be the key factor for the successful growth of a molecular line.[5] It was suggested that radical delocalization in the case of

† RIKEN.
‡ The University of Tokyo.

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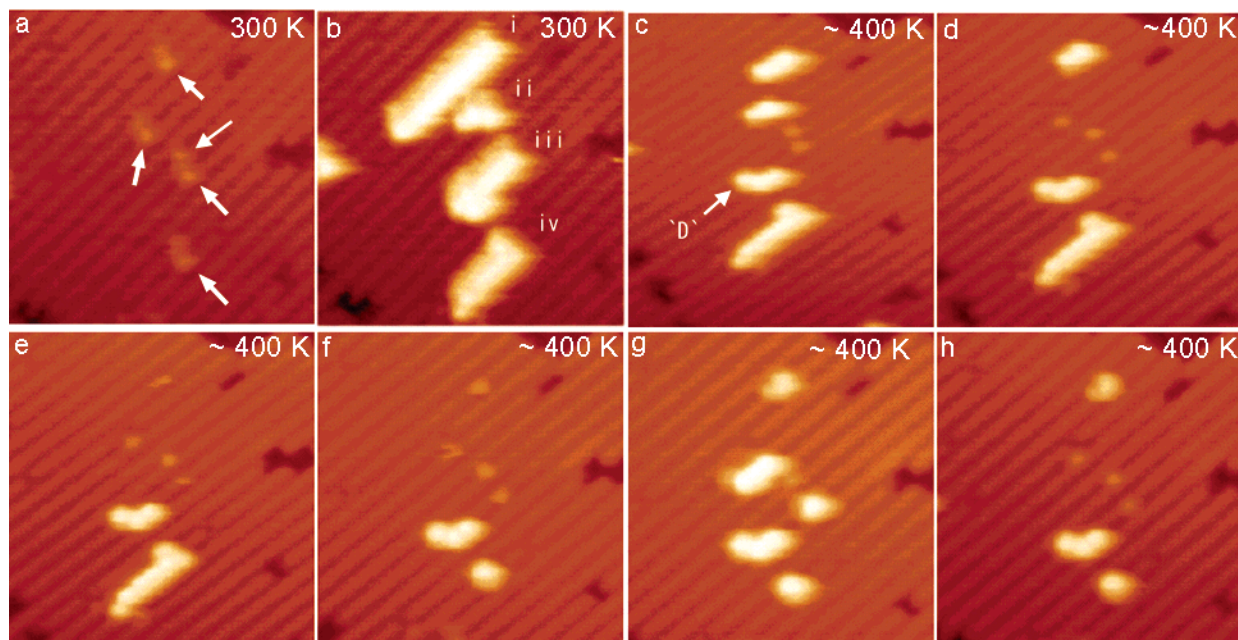

Figure 1. Series of STM images of the same area on the H-terminated Si(100)−(2 × 1) surface measured at 300 (a, b) and 400 K (c−h). (a) Five dangling bonds (DBs) indicated by arrows created using high-voltage pulse injection from an STM tip. The shadow feature of each DB is due to the tip artifact. (b) Surface a exposed to ∼3 L of styrene at 300 K. (c−f) Sequential STM images after the temperature of surface b increased to 400 K. (g) Surface f was exposed to ∼4 L of styrene at 400 K. (h) Surface 3 min after g. V_{sample} = −2.4 V; I = 0.2 nA; scan area = 11 × 12 nm^2. A little area mismatch in some images is due to thermal drift at 400 K.

styrene or dispersion interaction with the substrate in the case of long-chain alkenes (C_nH_{2n}, $n \geq 8$) can stabilize the intermediate radical for abstracting H to facilitate line growth.[5] However, these stabilization mechanisms cannot explain the successful growth of molecular lines of allylmercaptan and acetaldehyde.[2,11]

To date, there has been no direct study that measures the thermal stability of a molecular line with an end DB. Lopinski et al.[1] have suggested that a styrene line formed at 300 K is stable for up to 20 h, and a minority of styrene lines survive even after annealing the surface at ∼600 K. They estimated an activation barrier for the desorption of styrene molecules in a line of 1.15 eV.[1]

In this study, controlled experiments on 1D molecular lines of various molecules on the Si(100)−(2 × 1)−H surface are performed by scanning tunneling microscopy (STM) at various temperatures. We, for the first time to our knowledge, directly observe that the end DB of a styrene line can initiate a reversed chain reaction, leading to the desorption of all molecules in a line and leaving the DB at the dimer site where it was originally located before the line growth. Desorption events are observed to be zero-order with an estimated rate constant $k = 1.17 \times 10^{-2}$ s^{-1} at 400 K. The complete disappearance of a molecular line through reverse chain reactions suggests that the observation of a freshly fabricated molecular line by STM depends on the rate of desorption at a given temperature; i.e., if the desorption rate is so fast that all the molecules in a line desorb before the image is scanned, we will see no line in the STM image. As predicted, we observe the molecular lines of adsorbed 1-hexene and 1-heptene on the Si(100)−(2 × 1)−H surface by STM at ∼180 K because of the reduced desorption rate, despite the fact that those molecules show no line growth at 300 K.

Experimental Section

Experiments were performed in an ultrahigh-vacuum chamber with a base pressure lower than 6 × 10^{-11} mbar. A variable-temperature scanning tunneling microscope (Omicron VT-STM) was used. The B-doped silicon sample (0.01 Ω cm) was cleaned by prolonged annealing at ∼850 K (∼8 h), followed by repeated flashings at 1400 K. The clean surface was H-terminated by exposure to atomic H, which was generated by a hot W-filament (∼2100 K), at a surface temperature of ∼625 K. The freshly prepared H−terminated surface usually contained a dilute concentration of unpaired DBs resulting from the incomplete H-termination;[12] otherwise, DB at a predefined position is generated using an STM tip.[13] Styrene and 2,4-dimethylstyrene (DMS) were purchased from Aldrich. Allylmercaptan (ALM), 1-hexene, and 1-heptene were purchased from Tokyo Chemicals Industries Co., Ltd. (TCI). Those colorless liquid chemicals were purified by several freeze−pump−thaw cycles or by pumping out the vapor above the liquid phase. The molecules were dosed onto the silicon surface through an electronically controlled pulse-valve doser. The sample was cooled to 180 K by the controlled flow of liquid N_2. The number of molecules dosed is expressed in Langmuir (1 L = 1 × 10^{-6} Torr•s), which is estimated from the background pressure reading using a B.A. gauge during the exposure.

Results

Figure 1 shows a series of STM images measured at the same area of the Si(100)−(2 × 1)−H surface, where a,b and c−h were measured at 300 and 400 K, respectively. In Figure 1a, five DBs created by the STM tip are indicated. The shadow feature of each DB (in Figure 1a) is due to the tip artifact. When the surface (a) was exposed to ∼3 L of styrene at 300 K, four styrene lines (i−iv) with different lengths shown in Figure 1b were observed. Note that the styrene line initiated at a DB can

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give a single or a double line on the same dimer row.[1,3] The wider part of the line may be the double line. It was observed that the length of the styrene line does not decrease even after several hours at 300 K. In rare events, the length of a line is found to decrease at 300 K. Since all of these growing lines (Figure 1b) are not ended at any preexisting defects, it is expected that there is a free DB at the end of each line.

To see if the end DB of a line can initiate a reversed chain reaction to desorb styrene molecules in a line, we continuously scanned the same area while the temperature of Figure 1b gradually increasing to 400 K. Note that the time required to increase the temperature from 300 to 400 K was ~30 min to maintain tracking of the same scanning area. It was observed that the length of the above lines does not decrease until the temperature of the surface reaches to 400 K. Sequential measurements of STM images at 400 K (as shown in Figure 1c−f) indicate that the length of a styrene line gradually decreases to zero and leaves a DB at the same position (Figures 1c−f,h), where it was originally located before the line growth (Figure 1a). The feature indicated by "D" in c, which appeared by breaking line iii, shows no change throughout the experiment, and D's composition is not clearly understood. The residue of line iv in Figure 1f disappeared several minutes after the measurement of Figure 1h. When the surface f was again exposed to styrene molecules (~4 L) at 400 K, only very short lines of styrene were observed (Figure 1g), which ultimately disappeared within a few minutes (~5 min) after the formation of line (Figure 1h). Note that the fuzzy appearance of DBs in Figure 1e,f is possibly due to flipping of a DB on the same dimer at 400 K.

It has been reported that similar to the styrene molecule, 2,4-dimethylstyrene (2,4-DMS) also forms a molecular line along the Si-dimer row when exposed to the Si(100)−(2 × 1)−H surface containing unpaired DB sites.[3] To observe the effect of two methyl groups in a phenyl ring on the stability of the line, we monitored a newly formed DMS line for about 30 min at 300 K. Figure 2 shows the STM images of (a) the Si(100)−(2 × 1)−H surface exposed to ~1 L of DMS and (b) the surface a exposed to an additional ~4 L of DMS at 300 K. The images shown by Figure 2c and d were measured 3 and 9 min after measuring the surface b, respectively, without additional doses of DMS. A single DMS line was grown (Figure 2b) at the site indicated by the arrow in Figure 2a, and the single line indicated by "S" became a double line in Figure 2b. The time-dependent measurements (Figure 2c,d) indicate that the length of the single line decreased in Figure 2c,d. The decrease in the length of the DMS line with time at 300 K is observed to be reproducible. Further growth of the double line in Figure 2c is due to the reaction of DMS molecules from the background.

To determine the comparative stability of parallel-row styrene and cross-row ALM lines, we gradually increase the temperature of the surface containing both ALM and styrene lines (Figure 3a) to 400 K. Figure 3b shows the surface (a) measured at 400 K. Similar to that observed in Figure 1, most of the styrene lines became shorter at 400 K, as indicated by arrows (Figure 3a), whereas the ALM lines showed no change in length. In fact, the ALM lines are observed to be stable even at 650 K. The styrene lines that showed no change in length might have been stabilized by the termination of end DB by some means such as encountering with another DB (discussed in detail later).

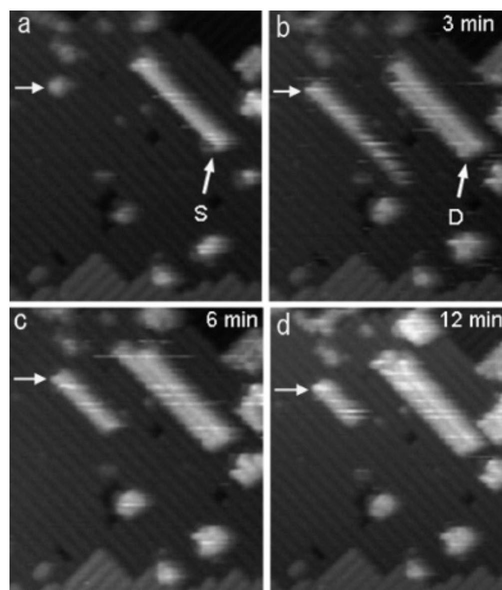

Figure 2. Selected area STM images of (a) the Si(100)−(2 × 1)−H surface containing dilute concentration of DBs exposed to ~1 langmuir of 2,4-dimethylstyrene (DMS) and (b) surface a exposed to an additional ~4 L of DMS at 300 K. Images b, c, and d are measured 3, 6, and 12 min after measuring surface a, respectively, without additional doses of DMS. The newly grown line (indicated in b) is observed to decrease in length in c and d. $V_{sample} = -2.0$ V; $I = 0.2$ nA; scan area = 15 × 18 nm^2.

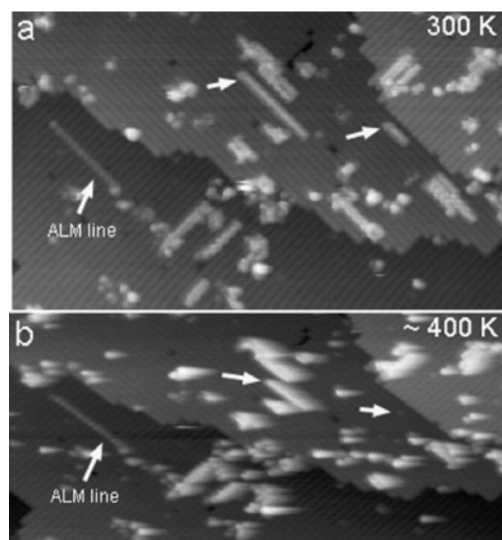

Figure 3. Selected same-area STM images of (a) the Si(100)−(2 × 1)−H surface containing some styrene and allylmercaptan lines at 300 K and (b) surface a after increasing temperature to 400 K. The vertical compression of the image in b is due to the thermal drift of the sample. $V_{sample} = -2.5$ V; $I = 0.2$ nA; scan area = 60 × 36 nm^2.

Discussion

As mentioned earlier, the initiation step of the chain reaction of styrene and other alkene molecules is the interaction of the >C=C< part with the DB of the substrate, which results in a C-centered intermediate radical, as shown in Figure 4a,b (in the case of styrene).[1,10] This intermediate radical (Figure 4b) abstracts a H from the nearest dimer in a row resulting in a new DB site (Figure 4c), which can react with another alkene molecule leading to a 1D molecular line. Computational studies have suggested that the stability of a C-centered radical and an adsorbed molecule adjacent to a DB is the key factor for the

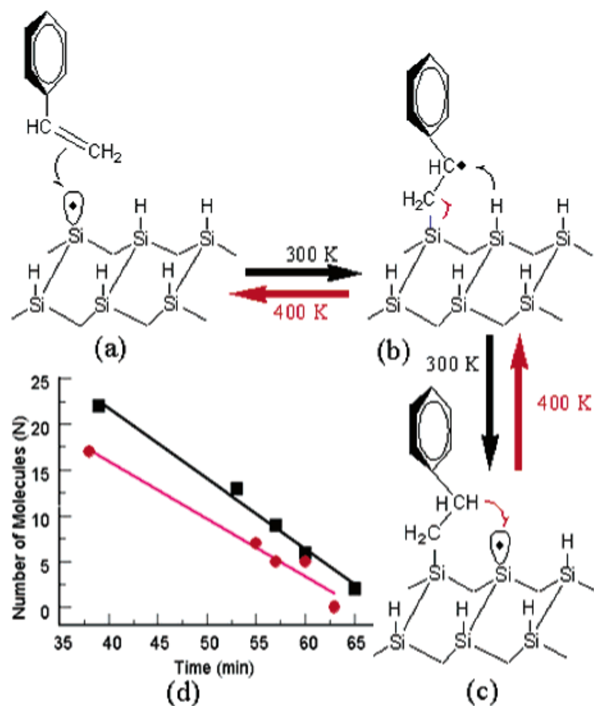

Figure 4. (a−c) Schematic of reaction mechanism for forward and reversed chain reactions of styrene molecules on H-terminated Si(100)−(2 × 1) surface at 300 and 400 K, respectively. (d) Change in number of molecules in two typical styrene lines as a function of time at 400 K. The solid lines are the linear fit to the data points for two different styrene lines.

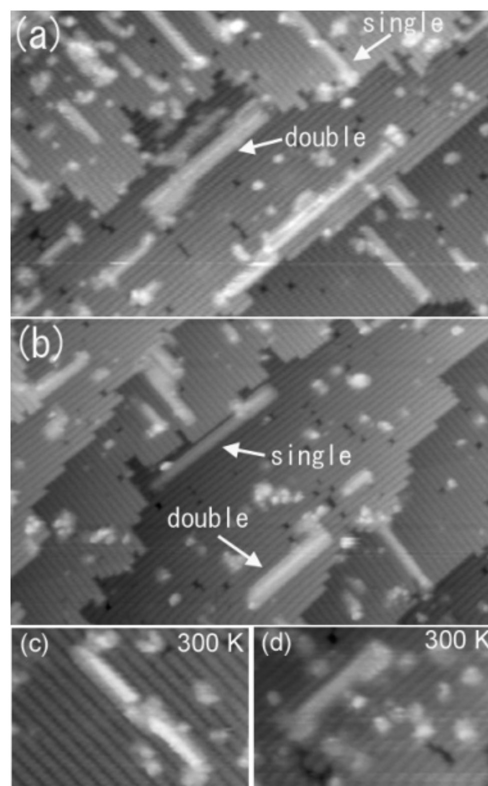

Figure 5. Selected area STM images of the Si(100)−(2 × 1)−H surface containing some molecular lines formed by DB-initiated chain reactions of (a) 1-hexene and (b) 1-heptene at 180 K. Typical single and double lines are indicated. The exposure of molecules for a and b are ∼2 and ∼8 L, respectively. (c) and (d) are STM images showing molecular lines of adsorbed 1-hexene and 1-heptene, respectively, after warming up the sample to 300 K. $V_{sample} = -2.5$ V; $I = 0.2$ nA; scan areas = (a) 48 × 30 and (b) 54 × 34 nm^2.

successful growth of molecular lines.[5,14,15] DiLabio et al.[5] have shown by calculation that the interaction of a styrene molecule with a DB (Figure 4b) is exothermic by 0.8 eV, and the subsequent H abstraction resulting in structure c further releases 0.1 eV of energy. Cho et al.[14] have obtained an adsorption energy of 0.55 eV for the intermediate state b, an energy barrier for H abstraction of 0.88 eV, and an activation energy for the reverse reaction from the final state (c) to the intermediate state (b) of 1.43 eV. Kang and Musgrave have reported adsorption energies of 0.98 and 0.96 eV for states b and c, respectively.[15]

The direct observation of the decreasing length of styrene lines at 400 K in the present study (Figure 1) indicates that molecules in a growing styrene line undergo desorption at 400 K. After the desorption, the appearance of DB at the dimer site where it was originally located suggests that desorption events occur through the chain reaction mechanism that is similar but reversed to the growth processes, i.e., a H from the adsorbed styrene goes back to the DB site (as indicated in Figure 4c) followed by the breaking of the Si−C bond (Figure 4b). The change in the number of molecules (N) in the styrene line as a function of time (t) is observed to be linear, as shown for the two different styrene lines in Figure 4d. The N vs t plots clearly suggest that desorption events of styrene molecules through the chain reaction mechanism is zero order; i.e., the rate of reversed reaction is independent of the number of molecules in a line. The observed zero-order reaction is consistent with the facts that the molecule at the next nearest neighbor site to the DB site plays no role in the desorption process of the molecule at the nearest neighbor site to the DB site. The slight slope difference between the two lines (red and black) is perhaps due to the difference in substrate temperature (±20 K).

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Employing the zero-order rate equation ($-dN/dt = k$) in Figure 4d, the average rate constant k for the reversed reaction at 400 K is estimated to be 1.17 × 10^{-2} s^{-1}. If the preexponential factor (ν) is assumed to be 10^{14} s^{-1} (as in ref 14), E_d is estimated to be 1.26 ± 0.06 eV. This estimated activation barrier for the reversed reaction lies within the calculated values (0.90−1.43 eV) reported earlier.[5,14,15] Compared with that in styrene line, the activation barrier for the reversed reaction in the 2,4-DMS line seems to be lower, as indicated by the frequent reversed reaction at 300 K. Neglecting the number of molecules adsorbed from the background in Figure 2b−d, the rate constant k for 2,4-DMS at 300 K is estimated to be 2.59 × 10^{-2} s^{-1} , which gives E_d values of 0.93 eV. This lower E_d for 2,4-DMS than that for the styrene line may be related to the steric crowding of two methyl groups in the phenyl ring.

Although the styrene and 2,4-DMS molecules in a line easily undergo a reversed chain reaction at a certain temperature, ALM molecules in a cross-row molecular line do not undergo any reversed reaction, which make the ALM line more stable than the styrene line. The difference in thermal stability between parallel-row and cross-row molecular lines may be related to the interdimer distance along and across the dimer rows and the underlying chain reaction mechanism.[2,3] In the case of ALM line formation, two additional steps, namely, tautomerism and intradimer DB diffusion, are expected to be involved in the reaction processes,[2] which makes the reversed reaction very unlikely.

The phenomena observed in Figures 1 and 2 suggest that the desorption rate at a given substrate temperature is crucial for molecular lines to be observed in an STM image. If the desorption rate is so fast that all the molecules in a line desorb before the image is scanned, we will see no line in the STM image, even if the molecules might have undergone a chain reaction and formed a line during the exposure. Thus, we predicted that alkenes (i.e., C_nH_{2n}, $n \leq 8$) that show no line growth at 300 K might show a molecular line in STM image at lower temperatures (<300 K) because of the reduced desorption rate. To realize our prediction, two typical alkene molecules, 1-hexene and 1-hepene, were studied at ∼180 K, and the results are shown in Figure 5. Similar to styrene[1] and long-chain alkene (C_nH_{2n}, $n \geq 8$),[5] 1-hexene and 1-hepene molecules also undergo a chain reaction initiated at unpaired DB sites on the Si(100)−(2 × 1)−H surface and form a stable molecular line at 180 K.

In agreement with previous report,[1] the present study suggests that if the end DB of a molecular line is removed by some means, the reversed chain reaction should not proceed, i.e., the thermal stability of a molecular line will be increased. There are a number of ways to remove an end DB, such as reacting with atomic H, encountering with a surface defect that quenches the radical, etc.[1] Thus, if the end DBs of the 1-hexene and 1-heptene lines are removed, molecular lines are expected to be observed even at higher temperatures (>180 K). In fact, some of the 1-hexene and 1-heptene lines formed at 180 K are observed in STM image even after warming the sample up to 300 K as shown in Figure 5c,d.

Conclusions

Controlled experiments on 1D molecular lines on the Si(100)−(2 × 1)−H surface have been performed using STM with various molecules at various temperatures. A continuous monitoring of some freshly prepared styrene lines during a gradual increase in surface temperature up to ∼400 K suggests that the end DB of a styrene line initiates a reversed chain reaction at 400 K, leading to the complete desorption of styrene line and leaves a DB at the dimer site where it was originally located. The change in the number of molecules in a line as a function of time suggests zero-order desorption kinetics with an estimated rate constant (k) of 1.17×10^{-2} s^{-1} at 400 K. In the case of 2,4-dimethylstyrene, a reversed reaction was observed even at 300 K. These observations suggest that the rate of desorption plays an important role in observing a molecular line by STM at a given temperature. Thus, we predicted that the molecular line of alkenes (i.e., C_nH_{2n}, $n \leq$ 8), which is not observed at 300 K, might be observed in an STM image below 300 K because of the reduced desorption rate. As predicted, we observed that 1-hexene and 1-hepene molecules underwent chain reactions initiated at unpaired DB sites on the Si(100)−(2 × 1)−H surface and formed stable molecular lines at 180 K. This observation suggests that the scope of forming the 1D molecular line on the Si(100)−(2 × 1)−H surface with various alkenes is much wider than that anticipated in previous studies. Compared with the styrene line, the cross-row allylmercaptan line is more stable.

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