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Ethyl iodide decomposition on Cu(1 1 1) and Cu(2 2 1)

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Abstract

Ethyl iodide decomposition on the Cu(1 1 1) and Cu(2 2 1) surfaces has been studied using thermal desorption spectroscopy and high resolution electron energy loss spectroscopy. On both surfaces ethyl iodide decomposes to produce ethyl groups and adsorbed iodine atoms. The ethyl groups decompose by β-hydride elimination to desorb as ethylene leaving adsorbed iodine atoms. The kinetics of β-hydride elimination on the Cu(2 2 1) surface are similar to those on the Cu(1 1 0) surface suggesting that the ethyl groups are reacting at the (1 1 0) step edges rather than on the (1 1 1) terraces. Vibrational spectra of the iodine atoms remaining on the surfaces after decomposition of the ethyl groups have been used to probe the iodine binding sites and to corroborate predictions based on density functional theory that the iodine atoms bind to the tops of the step edges. Iodine atoms on Cu(1 1 1) exhibit vibrational modes at 130 and 235 cm^{-1} that we assign empirically to in-plane and out-of-plane vibrations, respectively, of iodine atoms adsorbed at fcc sites on the (1 1 1) plane. On the stepped Cu(2 2 1) surface an additional peak appears at 80 cm^{-1} arising from iodine adsorbed at the step edges. The fact that this mode is at a lower frequency than the in-plane mode on the Cu(1 1 1) surface suggests that the iodine atom is adsorbed at the top of the step edge where its motion is unconstrained. These experimental results are consistent with the theoretical prediction that iodine atoms adsorb at the top of the step edges on the Cu(2 2 1) surface.

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1. Introduction

The chemistry of molecules on high Miller index surfaces with steps and kinks has been studied extensively for the purpose of understanding how defects influence surface chemical processes such as catalysis. These types of surfaces have structures consisting of low Miller index terraces separated by step edges as shown for the Cu(2 2 1) surface in Fig. 1. More complex structures can be prepared which have kinked rather than straight step edges. One interesting aspect of the chemistry of these surfaces is the site for adsorption of atoms and molecules. Clearly adsorbates have a far greater selection of possible adsorption sites than on low Miller index planes such as the Cu(1 1 1) surface. These sites are characterized by their different affinities for binding of adsorbates which will tend to reside in those with the highest binding energy. Comparison of CO adsorption on low and high Miller index Pt surfaces by Hopster and Ibach

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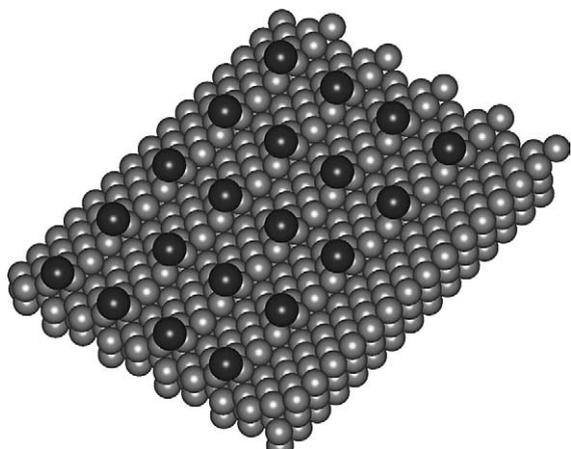
Fig. 1. The Cu(2 2 1) surface has (1 1 1) terraces that are three atomic distances in width separated by monoatomic (1 1 0) steps. The model of the Cu(2 2 1) surfaces illustrates a single iodine atom adsorbed at the top of the step edge as predicted by DFT calculations.

showed that the high Miller index stepped surfaces expose two additional adsorption sites for CO adsorption that do not exist on the flat low Miller index surfaces [1]. They proposed that one is on top of a step edge and the other is on the terrace near the step, in other words, at the bottom of the step edges. Both have higher binding energies than adsorption sites on the flat terrace. On stepped Cu surfaces, CO is probably the most widely studied adsorbate. CO preferentially adsorbs at step sites, with the carbon atom next to the Cu atom at the top of the step edge [2–5]. The goals of this study are to probe the sites for reaction of ethyl groups and the sites for iodine atom binding on the stepped Cu(2 2 1) surface.

The Cu(1 1 1) surface has a structure in which the surface atoms are in a single plane with the atoms in a hexagonal array. This surface exposes four high symmetry binding sites for adsorption: on-top, bridging, and the fcc and hcp threefold hollow sites. Iodine is known to adsorb in the fcc sites and to form a $(\sqrt{3} \times \sqrt{3})R30°$ ordered overlayer at a coverage of 0.33 monolayers (ML) [6–8]. The Cu(2 2 1) surface consists of (1 1 1) terraces separated by straight step edges with (1 1 0) structure (Fig. 1). This surface exposes adsorption sites on the terrace and a number of possible adsorption sites adjacent to the step edge. For the purposes of

this work we will limit them to three categories: terrace sites, sites at the top of the step edge and sites at the bottom of the step edge.

Recent density functional theory calculations have studied iodine adsorption on stepped Cu single crystal surfaces [9]. They showed that on surfaces with straight step edges iodine atoms bind most favorably at the top of the step edge with binding energies that are ∼29 kJ/mole higher than on the (1 1 1) terrace. Fig. 1 illustrates the iodine atoms bound to the top of the step edge. The vibrational frequencies of atoms on surfaces are sensitive to the sites at which they are bound. In order to corroborate the prediction of the density function theory, we have measured and compared vibrational frequencies of iodine atoms adsorbed on Cu(1 1 1) and Cu(2 2 1) using high resolution electron energy loss spectroscopy (HREELS). The vibrational spectra can shed light on the iodine adsorption sites on the stepped surface.

Alkyl groups and iodine atoms can be deposited on Cu surfaces by the dissociative adsorption of alkyl iodides. Lin and Bent studied the vibrational spectra of alkyl iodides decomposing on the Cu(1 1 1) surface and assigned a mode observed at 230 cm^{-1} to the Cu–I stretch mode with A1 symmetry. This mode can be thought of as the out-of-plane vibration in the sense that the motion of the iodine atom is along the surface normal. Theoretically we expect that the two degenerate in-plane modes (E symmetry) that are parallel to the surface should occur at a lower frequency for iodine atoms bound to the (1 1 1) terrace. The Cu(2 2 1) surface consists of (1 1 1) terraces separated by single atom steps with (1 1 0) structure, as shown in Fig. 1. One can imagine that iodine atoms could adsorb at either the tops or the bottoms of the step edges on the Cu(2 2 1) surface. The decrease in symmetry would remove the degeneracy of the two in-plane modes creating one that might be though of as parallel to the step edge and another that is perpendicular to the step edge but still roughly parallel to the plane of the surface. If the atom is adsorbed at the bottom of the step edge, its motion would be constrained and the in-plane mode perpendicular to the step edge would be expected to be higher in frequency than the in-plane mode on the Cu(1 1 1) surface. If the

atom is adsorbed at the top of the step edge, its in-plane motion ought to be less constrained than on the (1 1 1) surface and ought to appear at a lower frequency. Thus, the frequencies of modes observed on the Cu(2 2 1) can shed some light on the adsorption site of the iodine atoms. The conclusions of our work are that iodine atoms are sitting at the top of the step edges, as suggested by DFT simulations.

In this work we deposited iodine on the Cu surfaces by adsorption of ethyl iodide at low temperatures and subsequent heating to induce dissociation of the C–I bond depositing iodine atoms and ethyl groups onto the surface. Lin and Bent showed that on Cu(1 1 1), ethyl groups generated by dissociation of ethyl iodide decompose by β-hydride elimination resulting in the production and desorption of ethylene and hydrogen [10]. Jenks et al. studied the chemistry of ethyl iodide on Cu(1 1 1), Cu(1 1 0), and Cu(1 0 0) surfaces extensively with the purpose of understanding the influence of surface structure on reactivity [11]. They found that the kinetics of β-hydride elimination are substantially faster on the Cu(1 1 0) surface than on either the Cu(1 0 0) or Cu(1 1 1) surfaces. During temperature programmed desorption with a heating rate of 4 K/s, ethylene desorption was observed at 225 K on the Cu(1 1 0) surface but at 255 and 247 K on Cu(1 0 0) and Cu(1 1 1), respectively. The work reported here allows us the opportunity to study the kinetics of β-hydride elimination on the stepped Cu(2 2 1) surface and to identify the reaction site on the basis of the comparison with the three low Miller index surfaces. We find that the kinetics of β-hydride elimination on the Cu(2 2 1) are similar to those on the Cu(1 1 0) surface suggesting that the reaction is occurring at the (1 1 0) step edges on the Cu(2 2 1) surface.

2. Experimental

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 3×10^{-10} Torr. The UHV chamber was equipped with an Ar$^+$ ion sputtering gun, an LK-ELS3000 high resolution electron energy loss (HREELS)

spectrometer for obtaining adsorbate vibrational spectra, a quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD), and low energy electron diffraction (LEED) optics for surface structure determination. The Cu samples were mounted on a UHV manipulator and could be cooled down to 100 K and heated to 1200 K.

The surfaces were cleaned by cycles of 1.5 keV Ar$^+$ ion bombardment using a current of 6 μA and annealing to 920 K until no contaminants were detected by HREELS. This recipe was adopted from the procedure developed by Horvath to clean the Cu(6 4 3) surface [12]. The order and crystallinity of the Cu(1 1 1) and Cu(2 2 1) surfaces were verified by LEED. Ethyl iodide was adsorbed by exposure of the surfaces at low temperature to vapor introduced through a standard leak valve. Preparation of surfaces with iodine atoms alone was accomplished by adsorption of ethyl iodide followed by heating to 320 K to decompose and desorb the ethyl groups. Using HREELS and LEED, it was confirmed that this procedure removes all hydrocarbon fragments and leaves the surface modified by the presence of adsorbed iodine atoms.

The vibrational spectra were obtained using an LK-ELS3000 HREEL spectrometer. Each spectrum was collected with a dwell time of 0.7 s/channel and incident beam energies of 3.0 eV in a specular scattering geometry. The sample was held at ∼100 K while the spectra were being collected.

Ethyl iodide [C_2H_5I, 99%] was purchased from Aldrich Chemical Co. It was purified through several cycles of freezing, pumping, and thawing before introduction into the UHV chamber. The purity of ethyl iodide was verified by its mass spectrum.

3. Results

3.1. Ethyl iodide on Cu(1 1 1)

Ethyl iodide was adsorbed on the Cu(1 1 1) surface at 100 K and then decomposed by heating. On Cu(1 1 1), ethyl iodide is known to dissociate by cleavage of the C–I bond to produce adsorbed

ethyl groups and iodine atoms. The ethyl groups decompose by β-hydride elimination at 247 K to produce ethylene which desorbs immediately [11]. In other words the kinetics of ethylene production are rate limited by the β-hydride elimination step rather than the ethylene desorption step. Molecular hydrogen, the other product of the β-hydride elimination process, is known to desorb from Cu(1 1 1) at 300–400 K via the recombination of surface hydrogen atoms [13].

Fig. 2 shows TPD spectra obtained following ethyl iodide adsorption on Cu(1 1 1) at 100 K using increasing exposures. A signal at $m/q = 27$ ($C_2H_3^+$) was monitored during heating at 2 K/s. At the lowest exposure of 0.5 L a single desorption feature is observed at 247 K. The amount of ethylene desorbing at this temperature increases with
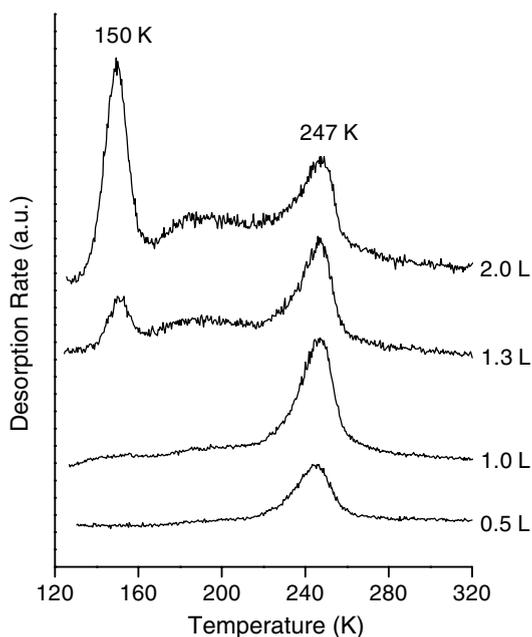
Fig. 2. TPD spectra of ethyl iodide adsorbed at 100 K on Cu(1 1 1) using various exposures. The peak at 247 K arises from ethylene desorption while the peak at 150 K is due to the desorption of molecular ethyl iodide. The appearance of the ethyl iodide desorption peak after an exposure of 1.3 L indicates that the ethyl iodide monolayer is saturated by an exposure of ∼1.0 L. Ethyl groups on the surface undergo β-hydride elimination to produce ethylene desorption at 247 K. The fragment monitored was $m/q = 27$ ($C_2H_3^+$). The heating rate was 2 K/s.

exposure until at 1.3 L the ethylene desorption feature saturates and a peak arising from ethyl iodide desorption appears at 150 K. This peak is due to multilayer desorption and increases indefinitely with increasing ethyl iodide exposure. These data indicate that an exposure of 1.0 L is sufficient to saturate the monolayer. We observe ethylene desorption at 247 K during β-hydride elimination of ethyl groups on the Cu(1 1 1) surface. This is identical to the temperature reported in a previous study of ethyl iodide decomposition on the Cu(1 1 1) surface [11]. It should be pointed out that in the previous work the heating rate was 4 K/s while it was 2 K/s in this work. In principle, the lower heating rate used in our work ought to result in a peak desorption temperature that is ∼5 K lower than that observed in the previous work. The fact that the two desorption temperatures are identical suggests some systematic differences in the two temperature measurements.

The adsorption of ethyl iodide followed by heating to 320 K leaves atomic iodine on the Cu(1 1 1) surface. LEED indicates that the iodine layer has a $(\sqrt{3} \times \sqrt{3})R30°$ structure (not shown in this paper) consistent with previous reports [7,8]. In Ref. [7], iodine was adsorbed on the surface by applying KI solutions to the Cu surface electrochemically. In Ref. [8], molecular iodine was adsorbed at room temperature. All results indicate that the decomposition of the ethyl iodide and elimination of the ethyl groups leaves atomic iodine on the Cu(1 1 1) surface.

The decomposition of ethyl iodide on the Cu(1 1 1) surface can be monitored by using HREELS to obtain vibrational spectra of the adsorbed intermediates generated by heating to different temperatures. Fig. 3 shows HREEL spectra of 1 ML of ethyl iodide on Cu(1 1 1) after heating to 100, 200 and 320 K. The vibrational mode assignments are summarized in Table 1. These assignments were made based on comparison with previous HREELS studies of ethyl iodide on Cu(1 1 1) [10] and Ag(1 1 0) [14], and the solid phase IR absorption spectra [15].

At 100 K we observe both the C–I stretch mode at 500 cm^{-1} and the Cu–I stretch at 235 cm^{-1}. Lin and Bent assigned the energy loss feature that they observed at 230 cm^{-1} following CH_3I adsorption
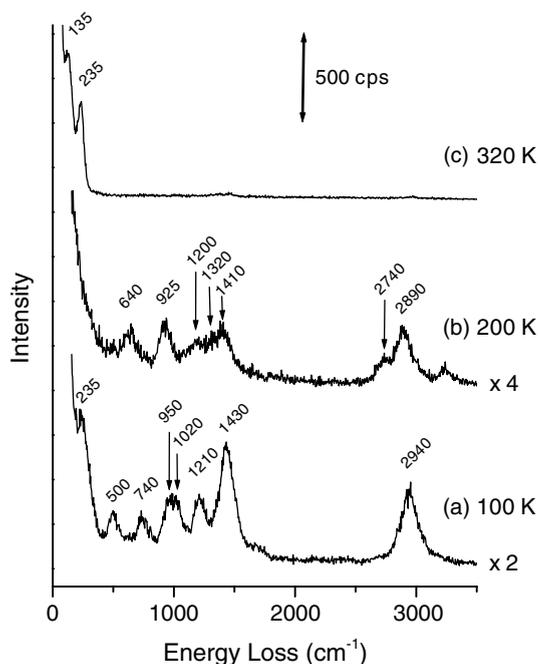
Fig. 3. HREEL spectra of the Cu(1 1 1) surface (a) after exposure to 1.0 L of ethyl iodide at 100 K, (b) after annealing to 200 K to form $C_2H_{5(a)}$ and $I_{(a)}$, and (c) after further annealing to 320 K to leave iodine only on the surface.

on Cu(1 1 1) to the Cu–I bond stretch mode [16]. Our result indicates that at 100 K the C–I bond remains intact in some but not all of the adsorbed

ethyl iodide. The HREEL spectrum in Fig. 2(b) shows the surface after annealing to 200 K. The most revealing feature of this spectrum is that the C–I stretch mode at 500 cm^{-1} has disappeared suggesting that all of the C–I bonds have been cleaved to form ethyl groups and iodine atoms adsorbed on the Cu(1 1 1) surface. In addition, most of modes have shifted to lower frequencies. The principle v_{CH} mode has shifted from 2940 to 2890 cm^{-1}. Lin and Bent observed this tendency in HREEL spectra of the Cu(1 1 1) surface following methyl iodide adsorption at 115 K and annealing to 180 K [16]. In their work, the most substantial change was the shift of the v_{CH} mode from 3045 to 2830 cm^{-1}. They pointed out that the frequency shifts can be attributed primarily to the change in surface coverage. We believe it is possible to interpret our results in the same way. In Fig. 2(b), the CH stretch mode at 2740 cm^{-1} is due to a softened CH stretch and has been observed before on Cu(1 1 1). It is known that some of the C–H modes in $C_2H_{5(a)}$ are softened and appear at 2745 and 2935 cm^{-1} and that the softened C–H bonds are those at the α-carbon bound to the surface [17]. The previous study suggested that charge donation from the metal to the anti-bonding orbital of the alkyl groups causes the C–H stretching mode-softening.

After annealing the ethyl iodide covered Cu(1 1 1) surface to 320 K, all CH$_x$ vibrational

Table 1
Vibrational modes and frequencies of ethyl iodide adsorbed on Cu(1 1 1) (cm^{-1})

Mode	1 L Cu(1 1 1)			1 L Cu(2 2 1)			4 L Cu(1 1 1)	1 L Ag(1 1 0)	Solid C_2H_5I
	100 K	200 K	320 K	100 K	200 K	320 K	120 K [10]	150 K [14]	IR [15]
Cu–I						80			
Cu–I			135			140			
Cu–I	235		235	240	215	235	230[a]		
C–I stretch	500			490					496
CH$_2$ rock	740	640		735	780		710	738	736
CH$_3$ rock	950	925		950	950		950	960	1049
C–C stretch	1020			1020			1046	1046	949
CH$_2$ wag	1210	1200		1200	1160			1187	1206
CH$_3$ sym. def.		1320						1366	1365
CH$_2$ asym. def.	1430	1410		1430	1420		1430	1427	1452
C–H stretch		2740					2745		
C–H stretch	2940	2890		2920			2935	2916	2968

[a] Mode for CH$_3$I/Cu(1 1 1) at 320 K [16].

modes disappear or become negligible as shown in Fig. 2(c). This is consistent with the TPD results showing that ethyl groups decompose to ethylene and desorb at 247 K. The only two substantial features remaining in the HREEL spectra are energy loss features at 130 and 235 cm^{-1}. We assign these two features to the Cu–I in-plane modes (E symmetry) and the out-of-plane stretching mode (A1 symmetry) respectively.

3.2. Ethyl iodide on Cu(2 2 1)

The mechanism of ethyl iodide decomposition is the same on the Cu(2 2 1) surface as on the Cu(1 1 1) surface although the kinetics of some steps differ. TPD spectra of ethyl iodide on Cu(2 2 1) are shown in Fig. 4. At an exposure of
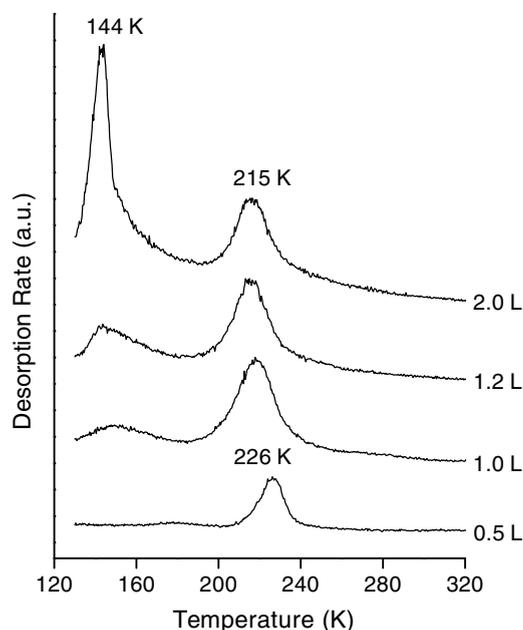
Fig. 4. TPD spectra of ethyl iodide adsorbed at 100 K on Cu(2 2 1) using various exposures. The spectrum obtained after an exposure of 0.5 L yielded an ethylene desorption peak at 226 K. At higher exposures the ethylene desorption peak shifts to lower temperatures reaching 215 K after an exposure of 2.0 L. Desorption of molecular ethyl iodide occurs at 144 K after an exposure of 1.0 L. The fragment monitored was $m/q = 27$ ($C_2H_3^+$). The heating rate was 2 K/s.

0.5 ML there is a single ethylene desorption features at 226 K. At higher exposures this feature shifts to 215 K and saturates in intensity. The origin of the desorption temperature shift observed here is not clearly understood at this point. At exposures above 1.0 L, a low temperature peak is observed at 144 K which arises from molecular desorption of ethyl iodide.

Ethylene is produced via β-hydride elimination in ethyl groups on Cu(2 2 1). The peak desorption temperature at 226 K is ∼20 K lower than on the Cu(1 1 1) surface. This indicates that the structure of the surface influences the kinetics of β-hydride elimination. This is not surprising since prior studies have shown that the kinetics of β-hydride elimination in ethyl groups on the three low Miller index Cu surfaces depend on surface structure. During heating at 4 K/s ethylene desorbs at 225, 247 and 255 K from the Cu(1 1 0), Cu(1 1 1) and Cu(1 0 0) surfaces, respectively [11]. These desorption temperatures imply barriers to β-hydride elimination of 65.0, 62.9 and 57.1 kJ/mole when analyzed via a simple Redhead analysis assuming a pre-exponential factor of 10^{13} s^{-1}. The ethylene desorption temperature of 226 K that we observe using a heating rate of 2 K/s on the Cu(2 2 1) surface indicates a barrier to β-hydride elimination of 58.7 kJ/mole. This value is closest to that observed on the Cu(1 1 0) surface. In fact the barriers to β-hydride elimination are identical on the Cu(2 2 1) and Cu(1 1 0) surface, if one accounts for the systematic 5 K difference in temperature measurements identified by comparison of the ethylene desorption temperatures on the Cu(1 1 1) surfaces. The fact that the kinetics of β-hydride elimination are identical on the Cu(1 1 0) and Cu(2 2 1) surfaces may be related to the fact that the step edge on Cu(2 2 1) has a (1 1 0) structure.

Vibrational spectra of ethyl iodide decomposition products on the Cu(2 2 1) surface have been obtained using HREELS. Fig. 5(a) shows the HREEL vibrational spectrum of 1 ML of ethyl iodide adsorbed on the Cu(2 2 1) surface at 100 K. The mode frequencies and assignments are summarized in Table 1. The 100 K spectrum is similar to that obtained on the Cu(1 1 1) surface at 100 K. The exception is a CO loss peak that appears at
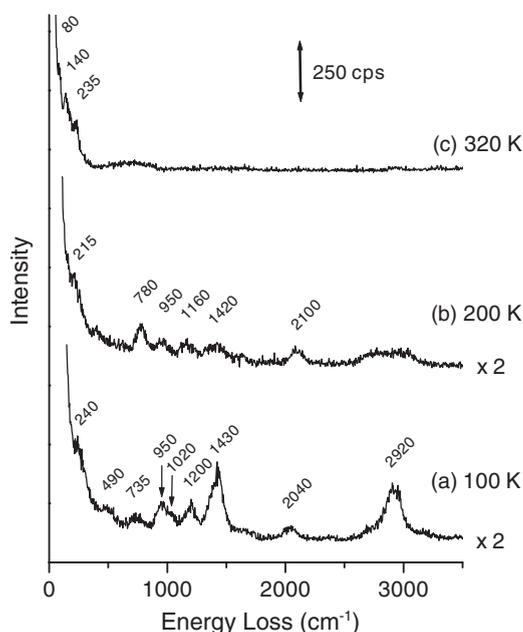
Fig. 5. HREEL spectra of the Cu(2 2 1) surface (a) after exposure to 1.0 L of ethyl iodide at 100 K, (b) after annealing to 200 K to form $C_2H_{5(a)}$ and $I_{(a)}$, and (c) after further annealing to 320 K to leave iodine only on the surface.

2040 cm^{-1} and arises from CO adsorbed from the chamber background. The feature at 240 cm^{-1} again is assigned to a Cu–I stretch mode. The presence of the feature at 490 cm^{-1} indicates that some C–I bonds are not cleaved at 100 K. Upon heating to 200 K, the overall signal intensities weaken. As in the case of the spectrum on the Cu(1 1 1) surface the ν_{CH} peak at 2920 cm^{-1} peak broadens. On the Cu(2 2 1) surface, it broadens to the point that no peaks are resolvable in the frequency range 2700–3000 cm^{-1} although energy loss features are clearly present in the spectrum. The poor resolution may well be due to the fact that the Cu(2 2 1) surface exposes a number of different adsorption sites and is thus more heterogeneous than the Cu(1 1 1) surface.

After heating the Cu(2 2 1) surface to 320 K, all the hydrocarbon vibrations disappear leaving only iodine vibrational modes at 80, 140, and 235 cm^{-1}. The feature at 80 cm^{-1} was not observed in the spectrum of I on the Cu(1 1 1) surface. This feature is, therefore, assigned to the vibration of iodine

atoms bound to the step edge on the Cu(2 2 1) surface.

4. Discussion

4.1. β-Hydride elimination on stepped surfaces

TPD measurements have been used to measure the kinetics of β-hydride elimination in ethyl groups deposited onto the Cu(1 1 1) and Cu(2 2 1) surfaces by dissociative adsorption of ethyl iodide. At a monolayer coverage of ethyl iodide, ethylene desorption is observed at 247 K from the Cu(1 1 1) surface and at ∼220 K from the Cu(2 2 1) surface during heating at 2 K/s. As mentioned above, prior work has shown that β-hydride elimination and ethylene desorption occur at 225, 247 and 255 K from Cu(1 1 0), Cu(1 1 1) and Cu(1 0 0) during heating at 4 K/s. Those measurements demonstrate that the barrier to β-hydride elimination on the low Miller index Cu surfaces is lowest on Cu(1 1 0) [11]. Comparison of the barrier to β-hydride elimination on the Cu(2 2 1) surface with those observed on the low Miller index surfaces shows that it is closest to that observed on the Cu(1 1 0) surface. As shown in Fig. 6 the Cu(1 1 0) surface structure has rows and troughs and that the step edge of the Cu(2 2 1) surface has a (1 1 0) structure. Based on the relationship between the kinetics of β-hydride elimination on the Cu(2 2 1) and Cu(1 1 0) surfaces, we infer that β-hydride elimination occurs at the steps rather than on the terraces of the Cu(2 2 1) surface. It may be that the ethyl group has to undergo less distortion at the (1 1 0) step edge to reach the transition state for β-hydride elimination than it does on the (1 1 1) terraces. Low energy electron diffraction has shown that ethylene, the product of β-hydride elimination in ethyl groups, adsorbs on the steps of the Cu(2 2 1) surface [18]. That study points out that the ethylene adsorption geometry on Cu(2 2 1) is very similar to that observed on Cu(1 1 0) [19]. Also previous STM measurements of ethylene on Cu(1 1 0) at 4 K showed that the molecules adsorb in the short bridge sites on the close-packed rows [20]. The fact that ethylene prefers to adsorb at the step edges on Cu(2 2 1) suggests that β-hydride
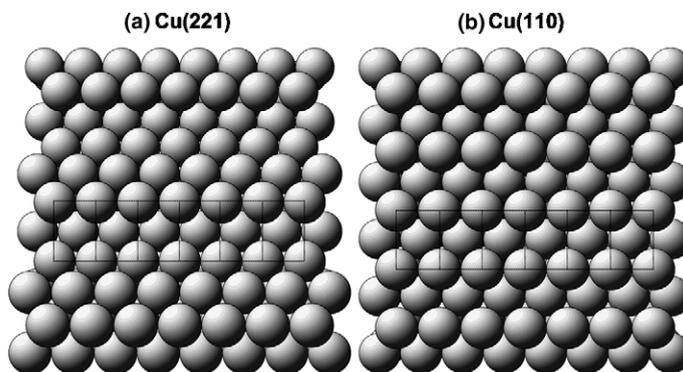
(a) Cu(221)   **(b) Cu(110)**

Fig. 6. Top view of the (a) Cu(2 2 1) and (b) Cu(1 1 0) surfaces. The step edge of the (2 2 1) surface has (1 1 0) structure.

elimination is thermochemically favored at the step edge by product stabilization. This, of course, makes the tacit assumption that the energetics of the reactant ethyl groups are identical on the terrace and the step edge.

4.2. Iodine adsorption sites on stepped surfaces

The primary goal of this work has been to compare the vibrational frequencies of iodine atoms adsorbed on the flat Cu(1 1 1) surface and the stepped Cu(2 2 1) surface in order to determine the iodine adsorption sites on the stepped surface. Fig. 7 shows the HREEL spectra of iodine on Cu(1 1 1) and Cu(2 2 1) in the frequency range 0–600 cm^{-1}. The highest frequency mode is observed at 235 cm^{-1} on both surfaces. This is assigned to the out-of-plane Cu–I mode. There are three vibrational modes for iodine atoms on the flat Cu(1 1 1) surface, which would be described as in-plane (two degenerate modes with E symmetry) and out-of-plane (A1 symmetry) vibrations. Empirically, we can predict that the out-of-plane mode appears at a higher frequency than in-plane modes. Thus, we can assign the energy loss feature at 235 cm^{-1} on the Cu(1 1 1) surface to the out-of-plane vibration and 130 cm^{-1} to the in-plane vibrations of iodine atoms.

In the vibrational spectra of iodine on the Cu surfaces there is an energy loss feature at 235 cm^{-1} which appears on both the Cu(1 1 1) and the Cu(2 2 1) surface. In addition there is a mode at 130 cm^{-1} on the Cu(1 1 1) surface that shifts to 140
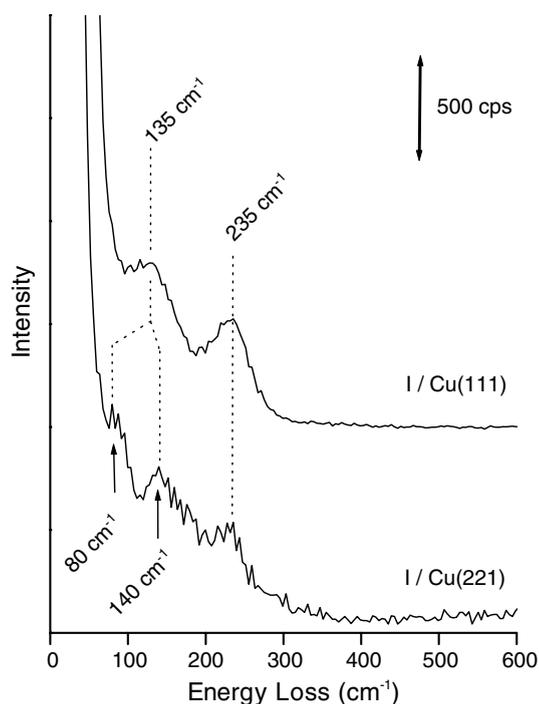
Fig. 7. HREEL spectra of iodine on the Cu(1 1 1) and Cu(2 2 1) surfaces. The 80 cm^{-1} loss peak is assigned to the vibration of iodine atoms adsorbed on the top of the step edges on the Cu(2 2 1) surface.

cm^{-1} on the Cu(2 2 1) surface. The most distinct difference between the HREEL spectra on the two surfaces is the appearance of a mode at 80 cm^{-1} on the Cu(2 2 1) surface that was not observed on the Cu(1 1 1) surface. Empirically one might expect

that if the iodine atom is adsorbed at the bottom of the step, the in-plane mode perpendicular to the step edge would be higher in frequency than the in-plane mode on the flat Cu(1 1 1) surface. Its motion perpendicular to the step edge would be constrained by comparison with its motion on the (1 1 1) surface. On the other hand if the iodine atom is adsorbed at the top of the step, one would expect that the frequency of the motion perpendicular to the step edge would be lower than that of the in-plane motion on the (1 1 1) surface. At the top of the step the motion is less constrained than on the (1 1 1) surface. The fact that we have observed a new mode on the Cu(2 2 1) surface at a lower frequency than the in-plane mode on the Cu(1 1 1) surface is consistent with the expectation that the iodine atom is adsorbed at the top of the step edge. This suggestion is consistent with the theoretical prediction that iodine atoms adsorb at the top of the step edges on Cu surfaces [9]. It seems that in many cases, the adsorption of atoms or molecules on the tops of step edges is favored over adsorption at the bottom of the step edge.

Using atomic vibrational frequencies to identify adsorption sites on surfaces can be complicated by the fact that the vibrational frequencies that one observes lie within the phonon bands of most metals. If the frequency of an adsorbate vibrational mode occurs below the maximum phonon frequency of the substrate, one cannot consider the adsorbate vibrational mode to be an isolated motion. Its motion will be coupled to the motion of atoms in the substrate. A prior study of chlorine atoms adsorbed on the Ag(1 1 1) surface has shown that the chlorine motion on the surface lies within the phonon band of the substrate. In that study, HREELS was used to show that chlorine adsorbed on Ag(1 1 1) showed an energy loss peak at 170 cm^{-1}. Calculations showed that a surface phonon mode of the Cl overlayer has a frequency of 167 cm^{-1} [21]. Ibach and Bruchmann showed that surface phonons of Ni(1 1 1) can be detected by dipole scattering in HREELS when appropriate coupling is provided by commensurate adsorbate lattices [22]. In their experiments, the presence of adsorbed oxygen, acetylene or hydrogen generated surface dipoles active to the HREELS dipole scattering mechanism. They observed an energy loss feature at $\sim$135 cm^{-1} that arises from a p(2×2) oxygen overlayer and another at $\sim$265 cm^{-1} that arises from a $(\sqrt{3} \times \sqrt{3})R30°$ oxygen overlayer. Previous HREELS experiments in an impact scattering geometry at three different beam energies and different scattering angles have measured frequencies of 107 and 228 cm^{-1} for the surface phonon modes of Cu(1 1 1) [23]. These are similar to the frequencies that we measure for energy loss features once iodine has been adsorbed on the surface. The implication of this is that the energy loss features that we observed may arise from motions that are more complex than the simple descriptions of the iodine atom motions that we have used to interpret our results.

5. Conclusions

Ethyl iodide decomposes on the Cu(1 1 1) and Cu(2 2 1) surfaces to deposit ethyl groups and iodine atoms. On the Cu(2 2 1) surface the ethyl groups undergo β-hydride elimination at the (1 1 0) step edges with a lower barrier than on the (1 1 1) terraces. The HREEL spectrum of iodine atoms on Cu(2 2 1) revealed an energy loss peak at 80 cm^{-1} that does not exist in the spectrum of iodine atoms on the Cu(1 1 1) surface. The frequency of this mode is lower than that of the in-plane vibrational mode of iodine atoms bound to the (1 1 1) terrace, suggesting that on the Cu(2 2 1) surface the iodine atoms are adsorbed at the top of the step edge.

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