Ethene Adsorption and Decomposition on the Cu(410) Surface

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The influence of open steps on the surface properties is shown by investigating the interaction of molecular ethene with Cu(410). We find a surprisingly low-temperature, site-selective chemistry at the strongly undercoordinated step sites. Ethene bonds either in a π-bonded or in a di-σ-bonded state or undergoes complete dehydrogenation. All pathways involve the low-coordination sites at the step, since the first species is partially stabilized with respect to low-Miller-index surfaces, while the other two are observed only on Cu(410). When annealing the surface, dehydrogenation and transformation into the di-σ-bonded moiety proceed, both processes being favored by faster heating rates. The so-generated carbon (presumably C_2 molecules) decorates the step edges, thereby blocking the active sites for subsequent dissociation and permitting only π-bonding of ethene. The dipole loss of carbon disappears in high-resolution electron energy loss spectroscopy when annealing to room temperature, indicating that carbon moves to more coplanar or even to subsurface sites where it still influences the surface chemistry. The surface reactivity is recovered when heating the crystal to 900 K since C dissolves then deep enough into the bulk.

1. Introduction

The improvement of industrial catalysts for heterogeneous reactions is strongly motivated by economical reasons. Knowledge-based designs to improve efficiency and/or selectivity may be achieved by a thorough fundamental understanding of the action of the catalyst. Using surface science methods and techniques, we can investigate the elementary steps, identify the active sites, and unravel the reaction mechanisms at the nanoscale. Although the importance of special surface active sites for catalysis has been known for many years, only a few investigations deal with the influence of under-coordinated sites on reaction selectivity.1,2 Controlling such a parameter is a central aspect for hydrocarbon chemistry on metal surfaces, which is important for both heterogeneous catalysis and nanotechnology. Carbon nanotube synthesis is based on the formation of C–C bonds and C–H scission,3 whereas the inhibition of carbon growth (C–C bond breaking) is important for preventing the poisoning of industrial catalysts.4 In the steam re-forming process, typically on Ni-based catalysts, hydrocarbons dissociate on the surface to form molecular hydrogen, and the remaining carbon reacts to produce carbon monoxide and additional hydrogen.4 However, a severe problem with nickel catalysts is that carbon can accumulate to form graphitic deposits, which ultimately deactivate the catalyst.1 For an improved catalyst, carbon removal should be facilitated, a process which would be thermodynamically favored by weaker metal–carbon bonding. Copper-based catalysts may be good candidates for achieving this goal, since the reactivity of copper exceeds that of silver and gold but is far lower than that of main-group transition metals. We focused our interest on the adsorption of a small hydrocarbon molecule, ethene, on Cu(410), a surface characterized by well-defined, open steps, organized in an ordered staircase.

It is known from previous work that ethene adsorbs reversibly on low-Miller-index Cu surfaces in a π-bonded state.5–7 However, recent studies showed that adsorption8 and decomposition9 can occur even on gold in the presence of defects (steps, adatoms, rough single crystals). Similarly, ethene was demonstrated to be stabilized at the open step edges of Ag(410),10 its adsorption energy being 3 times larger than on the (100) terraces. Detailed cluster calculations on the C_2H_4–Cu(111) interaction potential revealed two potential energy minima at different adsorbate-substrate distances, separated by an activation barrier.11 The first corresponds to the π-bonded species observed experimentally. The other is due to a strongly distorted, chemisorbed C_2H_4 moiety whose existence was excluded experimentally, at least for pristine Cu(111).5 The coexistence of such species was, however, suggested to occur for real systems11 and was experimentally observed to be possible for other sample preparation conditions.12 Di-σ-bonded ethene was indeed detected on Cu(100) as a result of photoinduced dissociation of CH_3I in temperature-programmed desorption (TPD) as evidenced by its higher (240 K) desorption temperature12 relative to that for the π-bonded form (120 K).5 In spite of the intensive studies of ethene adsorption on metal surfaces, this remains a complex system because a number of rather subtle factors determine the processes that actually occur, surface defects being just one of them.

In this paper, we investigate adsorption of ethene on Cu(410) at low temperatures by high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and TPD. The ethene bonding and reaction were analyzed as a function of temperature and coverage. While ethene is reversibly π-bonded on the (100)-like terraces, the step sites induce not only di-σ-bonding but also complete ethene...
molecules as well as their kinetic energy to be controlled. The temperature. The beam allows the direction of the gas-phase molecular beam in the temperature range from 125 K to room temperature. The beam allows the direction of the gas-phase molecules as well as their kinetic energy to be controlled. The rotational population in the beam is also very different for beam and backfilling experiments, since this degree of freedom is efficiently cooled by the adiabatic expansion occurring in the former case. The temperature dependence of the adsorbed layer was also monitored by HREELS, heating the crystal to the indicated temperature, and recording the spectrum after cooling the sample to the lowest temperature attainable in each experiment (from 125 to 150 K).

XPS and TPD investigations were performed at the University of Wisconsin—Milwaukee, using two different chambers. The sample cooling system typically allowed the sample to reach ~110 K. Exposures were performed at this temperature by backfilling only. The XPS chamber was operated at a base pressure of 7 × 10⁻¹⁰ mbar and equipped with a SPECS X-ray source and double-pass cylindrical mirror analyzer. Spectra were typically collected using a Mg Kα X-ray source, with 250 W power and an analyzer pass energy of 50 eV. Temperature-dependent XPS data were collected after increasing the sample temperature to 300 K and keeping it constant during the measurement. The TPD data were collected with a linear heating rate in another UHV chamber with base pressure of 7 × 10⁻¹⁰ mbar. The desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the sample and shielded from the rest of the chamber so that only molecules leaving the sample surface are detected. The chamber was also equipped with a double-pass, cylindrical-mirror analyzer for Auger electron spectroscopy and an ion gun for surface preparation.

The Cu(410) single crystal is a 10 mm diameter disk, oriented to within 0.1° of the (410) plane. The surface was prepared by cycles of sputtering with Ne⁺ or Ar⁺ ions followed by annealing for 3 min to ~900 K, until spectra indicative of the clean surface were observed by HREELS or by Auger spectroscopy. The surface geometry of Cu(410) is shown in Figure 1 and consists of three-atom-row wide (100) terraces alternating with monatomic steps running in the (001) direction and thus showing an open geometry.

3. Results

3.1. TPD Data. TPD spectra of deuterated ethene ($\text{CH}_2=\text{CH}_2$) from Cu(410) are presented in Figure 2 for sequential doses of 0.25 L performed by backfilling the chamber at a sample temperature of 110 K (1 L = 1 × 10⁻⁶ Torr s, equivalent to 0.15 ML; 1 ML corresponds on Cu(410) to 1.53 × 10¹⁵ molecules cm⁻²). The heating rate was 4.3 K/s up to a maximum temperature of 440 K. The spectra reported in panel a were collected by dosing the surface with ethene by backfilling, collecting the TPD spectrum, and then dosing the surface again without cleaning it. For the first dose, two well-defined desorption states are detected at ~143 and ~236 K. Note that the sharp onset of the low-temperature (~143 K) state suggests that the peak desorption temperature is less than 143 K. The well-separated peaks suggest that two distinct surface species are present. On the basis of previously published results, the low-temperature peak is associated with π-bonded ethene, while the feature at 236 K assigned to di-σ-bonded molecules.

Subsequent ethene doses result in a decrease in the intensity of the high-temperature peak and in the appearance of a desorption feature at lower temperature. No further changes were observed after six cycles. The ethene desorption states are then at ~143 and ~169 K, respectively. The sample was finally annealed to 900 K in vacuo, cooled to 110 K, and exposed again to ethene. The resulting TPD spectrum then recovered the shape observed for ethene desorption from the clean surface. The disappearance of the high-temperature feature indicates that ethene adsorption and desorption cycles modify the surface, deactivating the sites responsible for di-σ-bonding. It is evident from Figure 2b that heating to higher temperatures gradually restores the initial situation. Thus, the surface modification survives when annealing to 535 K, but it is eliminated when heating to 900 K. From the desorption temperature, the species leaving the surface at 169 K is reasonably ascribed to π-bonded ethene, but in another, more stable configuration. Most probably it consists of ethene located close to the deactivated step sites. As shown in the inset to Figure 2a, the TPD area is nearly constant for the latter state at 236 K. Note that...
Figure 3 displays TPD spectra for different exposures of ethene \((\text{C}_2\text{H}_4, \text{m/e}=27)\) on \(\text{Cu}(410)\) at 110 K by backfilling the chamber. The sample was cleaned by heating to 900 K and cooled again to 110 K before each dose. For the first dose (0.025 L), two desorption states are evident at 143 and 248 K. These peaks shift with ethene exposure to 148 and 223 K at the largest dose (1 L). The low-temperature peak, associated with \(\pi\)-bonded ethene, shows only a relatively small shift as a function of exposure, in accord with previous measurements on the ethene–\(\text{Cu}(111)\) system.\(^5\) The high-temperature feature appearing between 223 and 248 K is due to \(\delta\sigma\)-bonded ethene. The shift could be induced by carbon accumulation on the surface as a result of dehydrogenation at larger ethene exposures, since the data in Figure 2 show that the former has a strong influence on the second desorption peak.

For larger exposures, a gradual growth of both peaks was detected. Saturation of the high-temperature feature occurs at \(\sim 0.5\) L. The total TPD area is plotted in the inset of Figure 3 as a function of exposure. It reveals a linear increase in coverage with exposure, i.e., a constant sticking probability, in agreement with the results presented in the accompanying paper.\(^18\)

3.2. HREELS Data. To further investigate the nature of the ethene species on the surface, HREELS measurements were performed for ethene/\(\text{Cu}(410)\). The resulting spectra, presented in Figure 4, were recorded after dosing ethene by backfilling the chamber at various sample temperatures. The energy loss peaks at 935 cm\(^{-1}\) \([\nu_{(\text{CH}_2)}]\), 1290 cm\(^{-1}\) \([\nu_{(\text{CH}_2)}]\), 1569 cm\(^{-1}\) \([\nu(\text{CC})]\), 3018 cm\(^{-1}\) \([\nu_{(\text{CH}_2)}]\), and 3134 cm\(^{-1}\) \([\nu_{(\text{CH}_2)}]\) at 145 K are the signatures for \(\pi\)-bonded ethene,\(^5\) and the frequencies correspond to a \(\sigma\sim\pi\)-parameter of \(\sim 0.1\sim 0.2\).\(^19\) Since these experiments were performed by dosing at 145 K, these results are consistent with the presence of \(\pi\)-bonded ethene (Figure 2). Essentially no intensity is present at \(\sim 1150\) cm\(^{-1}\) \([\nu(\text{CC})]\)\(^20\) and \(\sim 2900\) cm\(^{-1}\) \([\nu_{(\text{CH}_2)}]\)\(^20\) (Figure 4 spectrum a), which would be typical of \(\delta\sigma\)-bonded ethene. This suggests that either the \(\delta\sigma\)-bonded species is initially absent on the surface and its formation is thermally activated or its intensity is too low to be detected. In order to check whether it forms at higher dosing temperatures, the surface was exposed to a larger dose of ethene at 193 K (Figure 4 spectrum b), a temperature at which most of the \(\pi\)-bonded moiety has already desorbed, while the \(\delta\sigma\)-bonded one should still be stable (see Figure 2). The resulting HREELS spectrum, recorded after cooling the sample back to 150 K, shows a broad feature at \(\sim 935\) cm\(^{-1}\), intensity at 1123 cm\(^{-1}\), and a peak at \(\sim 1330\) cm\(^{-1}\). The feature at \(\sim 935\) cm\(^{-1}\) is relatively insensitive to the hybridization state of ethene,\(^19\) but this mode is dominant in the case of \(\pi\)-bonding. As we will show later on and in the accompanying paper,\(^18\) two different \(\pi\)-bonded states, \(\pi_0\) and \(\pi_1\), characterized by different binding energies, must be present at the surface. Only \(\pi_1\) is, however,
molecular beam. This has the advantage of preserving a better vacuum in the sample chamber and decreases the readsorption probability. Since ethene was seeded in Ne, the molecules in the gas phase have the relatively low kinetic energy of 0.10 eV. The beam was incident at a grazing angle along the step down direction.

The spectrum obtained immediately after adsorption at 145 K shows the vibrational signatures of $\pi$-bonded ethene. As shown in Figure 5a on flashing to 250 K this moiety disappears while a loss at 1151 cm$^{-1}$, indicative of di-$\sigma$-bonded admolecules, is now apparent. These molecules leave the surface after heating above 250 K, in agreement with the TPD results of Figure 2. The 388 cm$^{-1}$ loss persists up to 500 K and thus cannot be due to ethene. Since no CH-related losses are observed upon annealing and since it is unlikely that the CC bond will cleave, we ascribe this mode to the C$_2$-substrate vibration, in accord with previous work. The higher kinetic energy of the impinging ethene, compared to backfilling, favors the dehydrogenation reaction when dosing at low temperatures.

An additional feature is observed in Figure 5 at 597 cm$^{-1}$. This energy coincides with that of H–Cu(100) and is therefore assigned to adsorbed hydrogen produced by the dehydrogenation reaction. This loss is strongly attenuated when heating to $\sim$190 K and disappears when heating to 270 K, indicating that either hydrogen desorbs in this temperature range or it moves subsurface.

From this analysis we may thus conclude that ethene dehydrogenation occurs and that the surface modification affecting the subsequent exposures of Figure 2 is due to carbon accumulating at the surface. The ethene losses in spectrum b of Figure 4 thus correspond to a mixed layer composed of both di-$\sigma$-bonded ethene and of $\pi$-bonded molecules stabilized by carbon, the latter corresponding to the desorption peak at $\sim$170 K in Figure 2.

Figure 5b also shows the effect of subsequent ethene doses, by using the beam at temperatures slightly higher than in the experiments reported in Figure 5a. Evidently, at this temperature the $\pi$-bonded species has already saturated after the first dose while the dehydrogenation process persists with exposure. After heating the sample, the vibrational signature for the di-$\sigma$-bonded loss is not as evident as in the experiment of Figure 5a. The reason for this apparent disagreement is, as will be shown below, that the conversion probability from $\pi$ to di-$\sigma$ depends both on dosing temperature and on heating rate, i.e., on the initial coverage of the $\pi$-bonded species and on the metastable population reached at high temperature when heating.

This effect is emphasized by the data displayed in Figure 6, where ethene is again dosed using the molecular beam. As can be seen, after annealing to 200 K, no ethene associated losses are observed when using a slow heating rate (0.3 K/s) and only the peak corresponding to C$_2$ survives. On the contrary, for the higher heating rate (1.5 K/s) the signatures of di-$\sigma$-bonded ethene, albeit weak, are present at 1151, 1360, and 2903 cm$^{-1}$. The larger intensity of the CH stretch, compared to the spectra in Figure 5, is due to the larger coverage of ethene achieved in this experiment, which may also explain the slightly different frequencies of $\nu$(CC) and $\nu$(CH$_2$) with respect to the experiment of Figure 4.

3.3. Dehydrogenation Kinetics. The picture that emerges is that ethene adsorbs at low temperatures predominantly in $\pi$-bonded states at terraces and at steps and that these admolecules either desorb or transform into more strongly
bound species upon heating: $\pi_0$ converts into $\sigma$ while $\pi_1$ dehydrogenates, leading to hydrogen and $C_2$ species. Dehydrogenation may take place also for the $\sigma$-bonded molecules. Since the formation of the $\sigma$-bond is not expected to favor dehydrogenation, the pathway from $\sigma$ to $CC$ is most probably indirect, involving step sites. This branching reaction can be explored by performing TPD experiments at different heating rates, and the results are displayed in Figure 7.
The apparent increase in desorption yield at higher heating rate arises because the time over which the data are collected is correspondingly shorter at higher heating rates. For the analysis of the spectra, the 32 amu (C₂D₄) desorption profile was fitted to the following analytical equation for the coverage during the desorption sweep appropriate for a first-order process:²⁵

\[
\Theta = \Theta_0 \exp \left( \frac{T_P^2}{T^2} - \frac{R}{T} \right) \exp \left( \frac{E_{\text{act}}}{R} \left( \frac{1}{T} - \frac{1}{T_P} \right) \right)
\]

where \( T_P \) is the peak temperature, \( E_{\text{act}} \) is the activation energy of desorption, and \( \Theta_0 \) is the initial coverage.

The desorption rate is then given by

\[
\text{rate} = k_1 \exp \left( -\frac{E_{\text{act}}}{RT} \right)
\]

where \( k_1 \) is the first-order desorption rate constant.

The first-order desorption profile is shown in Figure 7b, where the fitting variables are the desorption activation energy \( E_{\text{act}} \) (desorption) and the pre-exponential factor \( A \), using the experimental heating rate \( \beta \). These parameters were constrained to yield the experimental C₂D₄ desorption peak temperature (~238 K). The pre-exponential factor was allowed to vary to provide the best overall fit to the desorption profile to yield a value of \( \sim 7 \times 10^9 \text{ s}^{-1} \) and a desorption activation energy of \( 45 \pm 1 \text{ kJ/mol} \) (see Table 1).

This enabled the calculation of the relative coverage of C₂D₄ as a function of temperature during the desorption sweep.²⁵ The corresponding D₂ (4 amu) profile is displayed in Figure 7b. Ethene exhibited a small 4 amu signal in our mass spectrometer (~1% of the 32 amu signal) and the contribution due to C₂D₄ fragmentation is indicated. The difference between these curves and the experimental D₂ desorption profiles is due to hydrogen desorption from C₂D₄ decomposition. The D₂ desorption occurring between 220 and 260 K corresponds from the recombination of D formed during the ethene dehydrogenation process at that temperature, since hydrogen is then unstable, as demonstrated by HREELS (see Figure 5; the loss associated with hydrogen adatoms at 597 cm⁻¹ formed by lower T dehydrogenation disappears already below 190 K).

Since this deuterium is generated from di-σ-bonded ethene, the rate of its formation due to C₂D₄ decomposition, is given by

\[
\Theta(\text{C}_2\text{D}_4) = \text{A}_{\text{decomp}} \exp(-E_{\text{act}}(\text{decomp})/RT),
\]

where the C₂D₄ coverage during the desorption sweep is obtained for the C₂D₄ desorption profile as described above. The 4 amu profile was fitted by varying the pre-exponential factor, and the values of activation energy for decomposition to yield the values for each of the four different heating rates are listed in Table 1, and the resulting fit to the experimental desorption profile, including the sum of the fragmentation and decomposition, is shown in Figure 7a (- · -). The agreement with the experimental data is satisfying.

The relative 4 amu contribution due to decomposition at the surface (Figure 7a) increases with increasing heating rate, being nearly zero at a rate of 3.6 K/s and becoming eventually larger than the fragmentation peak at 10.4 K/s. This yields an activation

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**Figure 7.** (a) 4 amu (D₂) TPD profiles at various heating rates, including the results of fitting for D₂ due to fragmentation of molecularly desorbed C₂D₄ (- · · ·), surface decomposition of C₂D₄ (· · ·), and the total D₂ yield (· · ·), i.e., the sum of the fragmentation and decomposition profiles. (b) 32 amu TPD profiles of C₂D₄ on Cu(410) at various heating rates, including the analytical fits to first-order desorption described in the text.

**TABLE 1: Parameters Involved in the Fit of C₂D₄ TPD Data Shown in Figure 7a**

<table>
<thead>
<tr>
<th>Heating Rate/K s⁻¹</th>
<th>C₂D₄ Peak Temp/K</th>
<th>( A_{\text{desorb}} ) s⁻¹</th>
<th>( E_{\text{act}} ) (desorb.)/kJ mol⁻¹</th>
<th>( A_{\text{decomp}} ) s⁻¹</th>
<th>( E_{\text{act}} ) (decomp.)/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>238 ± 2</td>
<td>( 7 \times 10^9 )</td>
<td>46.0 ± 0.4</td>
<td>5 ± 4 \times 10¹¹</td>
<td>67 ± 3</td>
</tr>
<tr>
<td>4.3</td>
<td>237 ± 2</td>
<td>( 7 \times 10^9 )</td>
<td>45.4 ± 0.4</td>
<td>5 ± 2 \times 10¹¹</td>
<td>64 ± 2</td>
</tr>
<tr>
<td>8.6</td>
<td>237 ± 2</td>
<td>( 7 \times 10^9 )</td>
<td>44.1 ± 0.4</td>
<td>5 ± 1 \times 10¹¹</td>
<td>62.5 ± 0.5</td>
</tr>
<tr>
<td>10.4</td>
<td>240 ± 2</td>
<td>( 7 \times 10^9 )</td>
<td>44.3 ± 0.4</td>
<td>5 ± 0.5 \times 10¹¹</td>
<td>60.2 ± 0.2</td>
</tr>
</tbody>
</table>

* For comparison with ref 8, be reminded that 1 eV/atom = 96.485 kJ/mol.
energy for dehydrogenation of 63 ± 3 kJ/mol and a pre-
exponential factor of $\sim 5 \times 10^{11}$ s$^{-1}$.

This analysis implies that the dissociation efficiency increases
with heating rate, i.e., the conversion and dissociation processes
are linked, and that hydrogen is released during dissociation.
Indeed, as shown in Figure 5, hydrogen desorbs from Cu(410)
below 189 K, since the relevant loss at 597 cm$^{-1}$ is then no
longer present. This desorption $T$ is in accord with literature on
H/Cu(111)$^{26}$ and H/Cu(100)$^{27}$.

Additional evidence for ethene dissociation and carbon
caccumulation was obtained by XPS. In Figure 8, the carbon
coverage (in percent of monolayer of Cu atoms) is displayed
after someethene adsorption$-$desorption cycles, where the cover-
age is calculated from the relative integrated areas of C 1s and Cu
2p peaks and corrected for the relevant sensitivity factors. An initial,
very small amount of bulk carbon signal was subtracted from all
spectra. It can be seen that approximately half of the admolecules
dissociate during the first exposure$-$annealing cycle, while much
smaller additional carbon coverages accumulate for the subse-
quent doses, suggesting occupation of the reactive sites by the
dissociation products. The C 1s peak is at 284.5 eV (see inset
of Figure 8), which is consistent with the presence of C$_2$ species.
This binding energy could also be assigned to ethene, while
graphite and carbidic C are expected at 284 and 283 eV binding
energies, respectively. However, the presence of CH species is
excluded by the HREELS results.

3.4. Nature of the Ethene Desorption State on Carbon-
Contaminated Cu(410). To obtain additional insights into the
origin of 169 K desorption peak formed on a carbon-
contaminated surface (Figure 2), HREELS spectra were collected
for ethene adsorbed (dosed by backfilling) on carbon-
precovered Cu(410) surfaces. The result is displayed in Figure
9. Carbon contamination was achieved by repeated ethene
adsorption$-$desorption cycles as for the TPD experiments
(Figure 2a). The carbon-related loss is apparent at 367 cm$^{-1}$.
However, frequencies are evident at 942 and 1313 cm$^{-1}$, and
the frequency shift from 1290 to $\sim 1313$ cm$^{-1}$ suggests a slightly
higher $\sigma^-\pi$ parameter for ethene on a carbon-contaminated
surface.$^{19}$ This experiment allows us to conclude that the 169
K desorption peak in TPD spectra is associated with $\pi$-bonded
ethene. This is in accord with previous literature$^{22}$ for ethene
on carbon (or oxygen) precovered metals for which only
$\pi$-bonded configurations were reported.

Finally, we note that, at such a small dose by backfilling,
little or no dissociation takes place. The loss at 296 cm$^{-1}$
corresponds most probably to the ethene-surface vibration,
expected at this frequency for ethene at close-packed steps.$^{28}$
Dissociation is therefore favored at low coverage by the
relaxation of the step edge induced by carbon resulting from
previous uptakes. A similar phenomenon was reported for O$_2$
dissociation on Ag(210).$^{29}$

3.5. Identification of Dehydrogenation Sites. To further
investigate the path leading to ethene decomposition, we
performed HREELS investigations of ethene adsorption on bare
(after sputtering and annealing) and on CO-precovered (0.3 L)
Cu(410) surfaces. In both cases, identical exposures (1 L) of
ethene were used by backfilling the chamber. The crystal was
then heated to desorb both CO and ethene, which leave the
surface at almost identical temperatures. The normalized intensi-
ties of the low-frequency HREELS features, due to the remain-
ing carbon fragments, are presented in Figure 10. CO initially
adsorbs at the steps, where its binding energy is higher than on
the terraces, and the saturation CO coverage corresponds to 50% of
the step sites. If dissociation of ethene were to occur at
terraces, similar loss intensities would be expected in both
experiments. This is evidently not the case, since the loss due
to carbon fragments is at least three times more intense for
ethene adsorbed on the bare Cu (410) surface.

It can then be concluded that ethene dehydrogenates and leads
to carbon decorating the open step edges. Such carbon inhibits
further dissociative poisoning of the active sites and permits
adsorption only in the $\pi$-bonded state.

4. Discussion

The picture that emerges from the experiments is that ethene
adsorbs predominantly in a $\pi$-bonded configuration on Cu(410).
Figure 10. Normalized HREELS intensity measured on Cu(410) after dosing 1 L of ethene on bare Cu(410), followed by heating to 233 K (solid line), and after dosing 1 L of ethene on Cu(410) pre-dosed with 0.3 L of CO and heating to 204 K (dashed line). The slight difference in the C–Cu loss around 365 cm$^{-1}$ is connected to the different carbon coverage.

It desorbs from the terraces at $\sim$143 K, a value which compares well with that reported for Cu(100).16 More strongly bound $\pi$-bonded molecules sit at the undercoordinated Cu atoms at the steps, most probably in atop configurations by analogy to the case of ethene/Ag(410).10 Such molecules contribute to the high temperature tail of the desorption peak. Di-$\sigma$-bonded ethene is present, too, and desorbs30 at $\sim$240 K with an activation energy of $\sim$45 kJ/mol. Its site cannot be determined from the present data. Decomposition to C$_2$ species occurs, too, with an activation energy of $\sim$63 kJ/mol. The remaining carbon decorates the steps.

It is difficult to gauge the coverage of di-$\alpha$-bonded ethene, since it is evident in all spectra that the losses associated with it are weak compared to those of $\pi$-bonded ethene. At least at low exposure, the two populations should be comparable according to the TPD results (Figures 2 and 3). The different HREELS intensities may thus be due to different HREELS cross sections for the two forms of ethene, but this is not very likely. More probably, the difference corresponds to a smaller formation efficiency of the di-$\alpha$-bonded species at 145 K, the dosing temperature corresponding to the HREELS experiments, compared to 110 K, corresponding to the TPD results. To check this hypothesis, we exposed the sample to a large ethene dose (51 L) at 193 K, where mostly di-$\alpha$-bonded species would be expected from the TPD result. The outcome, reported in spectrum b of Figure 4, shows indeed only a very small loss associated to di-$\alpha$-bonded ethene. This result can be rationalized only assuming that the latter state is accessed through a precursor that becomes short-lived at the higher temperature. If formation of di-$\alpha$-bonds implies a precursor on the terraces (rather than at the steps), which is only slightly populated at 145 K, then only a very small amount of the former species will be produced in the HREELS experiments. The active site should, however, still be close to the step edge, since no $\sigma$-bonded ethene is reported for low-Miller-index Cu surfaces. A scheme of the complex potential energy surface resulting from our investigations is reported in the accompanying paper.18

A decrease in the ethene desorption yield is expected if carbon blocks the adsorption sites at the steps. This effect is not evident from the inset in Figure 2, in which the area under the TPD peaks is nearly identical for subsequent spectra, but it does occur when measuring subsequent ethene uptakes, as is shown in the accompanying paper.18 Ethene adsorption is thus hindered and di-$\sigma$-bonding is inhibited on the carbon-contaminated surface. Most probably, less stable adsorption sites close to the step become populated once the step itself is saturated by carbon atoms. This bond must be more stable than the $\pi$-bond in absence of carbon, since the desorption temperature of this moiety (169 K) is slightly higher.

As the heating rate of the TPD experiments was increased, the fraction of 4 amu (D$_2$) relative to 32 amu (C$_2$D$_4$) was found to increase, suggesting a pathway to surface decomposition of C$_2$D$_4$ in competition with desorption. These data were then fitted using a procedure to differentiate between D$_2$ due to the fragmentation of molecularly adsorbed C$_2$D$_4$ in the mass spectrometer and D$_2$ due to the decomposition of C$_2$D$_4$ on the surface. The results are listed in Table 1 and shown in Figure 7.

The variation in selectivity as a function of heating rate arises because of the widely varying kinetic parameters for desorption and decomposition. Transition-state theory indicates that the pre-exponential factor for desorption should equal $kT/h$, where $k$ is the Boltzmann constant and $h$ is Planck’s constant, if the partition functions of the adsorbate and transition state are identical. At the desorption temperature of $\sim$240 K, this yields a value of $\sim$5 $\times$ 10$^{13}$ s$^{-1}$, significantly larger than the experimentally derived value of $7 \times 10^{9}$ s$^{-1}$, implying that the transition state to desorption is significantly less mobile than the adsorbate and may suggest that desorption (as well as decomposition) is mediated by the steps.

A simple thermodynamic calculation, reported in the Supporting Information of ref 13, allows the magnitude of the C–Cu bond strength to be estimated. It shows that to render ethene dissociation on copper thermodynamically possible, the C–Cu binding energy should be larger than 170 kJ/mol. For comparison, the bond energy of C on Ni(100) was estimated from calorimetric experiments to be $\sim$203 kJ/mol.31 On the other hand, the calculated dissociation energies of monocarbides32 of Ni and Cu are $D_d$ (NiC) = $\sim$381 kJ/mol and $D_d$ (CuC) = $\sim$230 kJ/mol. The average binding energy of carbon adsorbed on copper as a result of ethene dissociation should thus be larger than 170 kJ/mol but smaller than 230 kJ/mol. These limits should be compared to the C–Ni binding energy, which lies between 203 and 380 kJ/mol. Since Ni is used as catalyst for the steam re-forming process, our study indicates that copper-based catalysts could work as well if open step edges are present. As demonstrated elsewhere, the under-coordination induced by roughening Cu(111) surfaces by ion bombardment at 145 K and by Cu atom evaporation at 90 K is still insufficient for activating ethene dehydrogenation28 and also to allow for di-$\sigma$-bond formation. It is, however, sufficient to stabilize $\pi$-bonded ethene. The steps generated by the latter procedures must, therefore, be mostly compact and thus different from the open ones of Cu(410).

On the basis of the presented results, we can summarize the processes occurring for ethene on Cu(410). The molecule may adsorb either as $\pi$-bonded or as di-$\sigma$-bonded or undergo complete dehydrogenation. The final state depends on adsorption
site, dosing temperature, and surface treatment. The π-bonded molecules are at the terraces as well as at the steps, while di-σ-bond formation and dehydrogenation occur only close to or at the open steps. When dosing at 110 K, the ratio between π- and di-σ-bonded molecules is close to unity until the steps become saturated. Further exposure at 110 K results only in molecules in their π-bonded state. Dosing at higher temperatures (145 and 193 K) on clean Cu(410) results in π- and di-σ-bonded molecules, too. However, the amount of the latter species is smaller when dosing at 110 K. This result indicates that the formation of di-σ-bonds is mediated by a weakly bound precursor. Dehydrogenation of ethene is less temperature dependent and occurs even at 193 K, however, not at room temperature (Figure 4), indicating that it is precursor-mediated, too. The process takes place at the step edges and this reaction is poisoned by carbon accumulation at such sites.

The dehydrogenation reaction can also be inhibited by preadsorbing molecules such as CO that compete for the step sites. Upon annealing the crystal to 900 K, carbon can diffuse into the subsurface region recovering the initial reactivity of clean Cu(410). The possibility of dehydrogenation occurring directly during the collision of ethene molecules with the surface is poisoned by carbon accumulation at such sites.

The additional dissociation process taking place during the TPD heating during the desorption of the di-σ-bonded layer, demonstrated by the dependence of the D₂ desorption yield on the heating rate, is less easy to rationalize. The breaking of a σ-bond occurring in di-σ-bonded molecules is close to unity until the steps become saturated. Further exposure at 110 K results only in molecules at the step edge. As soon as the surface becomes covered by carbon, the adsorption of ethene results in smaller and smaller amounts of di-σ-bonded molecules. One might expect a slight decrease in the ethene adsorption yield with carbon precoverage, if it blocks the adsorption sites. However, this is not the case, at least at low exposures. Ethene adsorption is still possible, albeit only in the π-bonded state. Most probably adsorption sites close to the step become populated once the step itself is saturated by carbon. This bond is more stable than the π-bond on the terrace and results thus in a slightly higher desorption temperature.

5. Conclusions

Our data demonstrate low-temperature site-selective chemistry of ethene on strongly under-coordinated sites on copper surfaces. On Cu(410) they induce not only di-σ-bonding but also promote complete dehydrogenation at low temperature. No partially dehydrogenated radicals could be detected. The so-generated carbon decorates the step edges, thereby blocking the active sites for subsequent dissociation and/or adsorption in the di-σ-bonded state. However, the dehydrogenation activity can be restored merely by heating the sample to 900 K. This fact and the smaller C–Cu bonding energy compared to C–Ni make Cu-based catalysts interesting for steam re-forming processes.