Dynamics of Ethene Adsorption on Clean and C-Contaminated Cu(410)

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As recently established (J. Am. Chem. Soc. 2008, 130, 12552), ethene adsorption on Cu(410) occurs both molecularly and dissociatively, the latter resulting in carbon contamination of the surface. Here we report on the coverage-dependent dynamics of C2H4 adsorption on clean and carbon-contaminated Cu(410). For the bare surface, the initial sticking probability has a very weak dependence on kinetic energy and is almost independent of angle of incidence. Molecular adsorption is in both cases precursor-mediated and nonactivated. Ethene dissociation takes place during adsorption as well as upon annealing. Both paths proceed via a molecular precursor. The former is translationally activated, while the latter depends strongly on the heating rate. The presence of preadsorbed carbon, resulting from previous uptakes, affects both the sticking probability and the attained saturation coverage. The latter quantity is shown to be a sensitive probe of carbon precoverage. A scheme of the complicated potential energy surface of this system is derived and discussed.

1. Introduction

A detailed understanding of surface dynamics is of crucial interest to properly model the properties of real catalysts and to obtain reliable estimates of reaction rates. This has prompted molecular beam reactivity studies over wide ranges of translational energies and angles of impingement for a number of gas/surface systems. To date, efforts were nevertheless mostly concentrated on low Miller index single crystal surfaces. Much less has been done about surfaces involving defects such as steps and kinks, although they are present on catalysts and were often shown to play a key role in the reaction dynamics because of the significant corrugation of the surface potential they produce and of the under-coordination of some of the atoms.1

The reactive adsorption of ethene on copper is such a case in which reactivity was demonstrated to be profoundly modified by steps. On all low-index surfaces,2–6 vibrational spectra of adsorbed ethene are indicative of π-bonded species. In the case of Cu(100), desorption was shown to occur at 140 K for a heating rate of 2.5 K/s,4 ethene is more strongly bound on Cu(410), a vicinal surface of Cu(100), on which a selective chemistry occurs.3,8 A combined analysis by high-resolution electron energy loss spectroscopy, thermal desorption, and photoemission spectroscopy showed that di-σ-bonded species are formed on the step edges and also dehydrogenation occurs. The importance of the change in surface chemistry is illustrated (a) by the presence of a shoulder in the desorption peak of π-bonded ethene, which extends up to 200 K at a heating rate of 3.6 K/s, (b) by the occurrence of an additional desorption peak around 240 K for C2H4/Cu(410), and (c) by the gradual change in the desorption spectra of subsequent adsorption experiments performed without sputtering the surface. The first point indicates that some π-bonded molecules are stabilized at the undercoordinated sites at the step edges; the second that a di-σ-bonded moiety forms; and the third that carbon accumulation, resulting from ethene dissociation, occurs.7,8

Beyond the overall step-induced changes in reactivity of the copper surfaces, questions arise about the dynamics of ethene/Cu(410) from a series of experiments which some of us performed for O2/Cu(410). Dissociative oxygen chemisorption9 as well as initial oxidation10 came out thereby to be anisotropic, being different for molecules impinging step up or step down.

The present paper is aimed at exploring such anisotropy in the dynamics of ethene adsorption on Cu(410) by dosing the surface with a supersonic molecular beam impinging at different angles, from step up to step down, and investigating the effects of kinetic energy and of the presence of preadsorbed carbon resulting from previous uptakes.

2. Experimental Details

Experiments are performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1 × 10−10 mbar, equipped with a supersonic molecular beam (SMB), a quadrupole mass spectrometer (QMS) not in line of sight with it (used for detection of beam molecules reflected off the surface), low-energy electron diffraction optics, a cylindrical mirror analyzer for Auger spectroscopy, and all other typical UHV facilities.11 The sample is a 10 mm diameter disk cut within 0.1° from the (410) plane. The Cu(410) surface consists of three lattice spacing wide (100) terraces separated by (110)-like monatomic step rises. Ethene adsorption leads to the formation of several coexisting moieties, namely π-bonded, di-σ-bonded, and carbon resulting from total dehydrogenation.7 Removal of the molecular species can be obtained by annealing above the respective desorption temperature. Elimination of carbon requires sputtering (performed at 25° off normal with 1.5 keV Ne+ ions) followed by flashing to 900 K. Annealing the ethene covered surface to 900
uptake does not necessarily imply a difference in the real saturation coverage, since uptakes are evaluated by integration and the integral can be extended only as long as the sticking probability is large enough to be measurable by KW (with the present signal-to-noise ratio, until $S \sim 0.02$). Above this point, $S$ is no longer measurable but the uptake may continue slowly up to the real saturation coverage, provided the exposure lasts long enough. In the following we shall then address the coverage at which $S$ is no longer measurable with KW as apparent saturation coverage.

In the experimental setup, the angle $\theta$ at which the beam impinges on the surface can be varied in the plane perpendicular to the steps and is measured with respect to the normal to the surface. The positive (negative) values correspond to step up (down). Herein, $\theta$ is explored from $+55^\circ$ to $-60^\circ$ (see Figure 1). Since the surface makes an angle of $14^\circ$ with the (100) terraces, the angular directions $\theta = +31^\circ$ and $-14^\circ$ correspond to normal incidence on the step risers and on the (100) nanofacets, respectively (see inset of Figure 1B).

3. Results

3.1. Ethene Adsorption on the Bare Cu(410) Surface.

Figure 1 shows the result of KW measurements recorded during the exposure of ethene on Cu(410) at a temperature $T = 145$ K, with $E_i = 0.10$ eV (Figure 1A) and $E_i = 0.36$ eV (Figure 1B).

The following points should be noted:

(1) The initial sticking probability, $S_0$, depends little on $E_i$ and $\theta$.

(2) At $E_i = 0.10$ eV, $S$ remains constant for several seconds, while at $E_i = 0.36$ eV it increases initially. It eventually decreases abruptly in both cases.

(3) When the surface is close to saturation and the exposure is stopped by intercepting the beam with the inert flag in the experimental chamber, an increase of the C$_2$H$_4$ partial pressure above the steady state level is observed.

(4) At $E_i = 0.10$ eV, the uptake is significantly larger for $\theta = -60^\circ$ than for $\theta = +45^\circ$, while at $E_i = 0.36$ eV this difference is definitively smaller. Note that the effect is due to the stable fraction since the difference persists after subtracting the contribution of the metastable species.

This result is highlighted in Figure 2, which reports the attained surface coverage vs time.

Outcomes (2) and (3) are expected and have been reported already, e.g., for C$_2$H$_4$/Ag(410)$^{13}$ and C$_2$H$_4$/Ag(210)$^{14}$. In particular, outcome (2) indicates that an extrinsic precursor is active both at thermal and hyperthermal energy. The increase of $S$ with coverage at hyperthermal energy has been traditionally explained with a mechanical effect known as adsorbate-assisted adsorption$^{15}$, according to which ethene molecules hitting on preadsorbed companions are able to more efficiently dissipate their excess energy due to the better mass matching. The phenomenon was not, however, observed for some systems showing a nearly perfect mass matching$^{16}$. This observation led to the alternative hypothesis that the increase of $S$ is connected to an adsorbate-induced enhancement of the corrugation of the gas-surface potential$^{17}$. The latter enables an easier conversion of the normal momentum of the impinging molecule into parallel momentum. As we will show later on, this is most probably the relevant physics for the present system.

Result (3) implies that, at $T = 145$ K, some of the adsorbed molecules are in a metastable state in equilibrium with the beam pressure$^{1}$. We identify such molecules with ethene at the terraces, which is known to be unstable at the temperature of
and in He ($E_i$).

The energy and angle dependence of the saturation coverage ($S_0$) is nearly independent of $E_i$ and $\theta$ (see also Figure 3). The ineffectiveness of kinetic energy is surprising for nonactivated adsorption, for which $S_0$ usually decreases markedly with increasing translational energy. The independence of $S_0$ on $\theta$, on the other hand, is expected as long as the normal energy of the molecules is small compared to the depth of the chemisorption well, while in the present case, it is observed also at high kinetic energy. We shall come back to this point later on in the paper.

The energy and angle dependence of the saturation coverage (point (4)) is at variance with previous observations on the (otherwise similar) $\text{C}_2\text{H}_4/\text{Ag}(410)$ system, for which it depends on $\theta$ at all energies and is largest when impinging step up. The

Next we comment on the coverage dependence of $S$. If the ethene dissociation probability (and hence carbon contamination) while dosing and annealing to 273 K were small, we would expect a subsequent ethene uptake (on the C-contaminated surface) to nearly superimpose with the one performed on the clean surface. This is approximately the case for

$S(\Theta)$ curves for $E_i = 0.10$ eV (left) and 0.36 eV (right) and for several angles of incidence are shown in Figure 3. The total uptake at 0.10 eV is larger when impinging step down ($\theta = -60^\circ$, red) than step up ($\theta = +45^\circ$, blue), a difference that disappears already below 170 K (data not shown). Since at $\theta = -60^\circ$ the step rises are completely in shadow, the additional coverage must be at the upper side of the step, which can be more easily reached by molecules impinging step down if they keep at least partial memory of the direction of their parallel momentum in the gas phase. No angle dependence of the total saturation coverage is present, within the experimental error, for doses performed at $E_i = 0.36$ eV.

The initial sticking probability $S_0$ vs $T$ is reported in Figure 4 for the He seeded beam at normal incidence. $S_0$ decreases with $T$ so that no adsorption is observed when dosing at room temperature. This dependence indicates that all pathways, including the dissociative one, are precursor mediated. If a direct path is present, then its contribution is lower than the sensitivity of the King and Wells’ method.

### 3.2. Ethene Adsorption on C-Covered Surfaces

All the experiments reported so far were performed on the freshly sputtered surface, i.e., in absence of carbon contamination. In the following, we investigate the effects on the ethene adsorption dynamics of residual carbon. We shall refer to “clean” or “carbon-contaminated” to indicate surfaces prepared, respectively, by ion bombardment and annealing to 900 K or surfaces pre-exposed to $\text{C}_2\text{H}_4$ up to saturation and annealed to 273 K. Two heating rates were employed for annealing to this $T$: the former, denoted as “slow”, takes ~5 min, while the latter, denoted as “fast”, takes only 1 min and implies the use of electron bombardment on the back of the sample. The average heating rate reads then 0.3 and 1.8 K/s.

In Figure 5 we compare the $\text{C}_2\text{H}_4$ uptakes performed with $E_i = 0.10$ and 0.36 eV on clean and carbon-contaminated Cu(410). First of all, we note that the initial sticking probability for the latter case is larger than for the clean surface. This agrees with TPD results reported in ref 8 showing an increased total uptake for very low subsequent exposures of 0.25 L ethene by backfilling, when the sample is cleaned only by a rapid annealing to room temperature (without sputtering) after each dose. The presence of preadsorbed carbon increases, therefore, the sticking probability.

In our experiment, we shall denote $\Theta$ as the coverage corresponding to the total uptake, which is defined as including both stable and unstable species.

Outcomes (1) and (4) are new and unexpected. The former indicates that, as long as only the interaction with the bare surface is concerned, $S_0$ is nearly independent of $E_i$ and $\theta$ (see also Figure 3). The ineffectiveness of kinetic energy is surprising for nonactivated adsorption, for which $S_0$ usually decreases markedly with increasing translational energy. The independence of $S_0$ on $\theta$, on the other hand, is expected as long as the normal energy of the molecules is small compared to the depth of the chemisorption well, while in the present case, it is observed also at high kinetic energy. We shall come back to this point later on in the paper.

The energy and angle dependence of the saturation coverage (point (4)) is at variance with previous observations on the (otherwise similar) $\text{C}_2\text{H}_4/\text{Ag}(410)$ system, for which it depends on $\theta$ at all energies and is largest when impinging step up. The

Figure 2. Ethene uptake curves obtained from the data of Figure 1. The highest coverage reached corresponds to the total uptake, $\Theta$, while the asymptotic value after the flag intercepts the beam again corresponds to the stable coverage.

Figure 3. Sticking vs coverage for 4\% $\text{C}_2\text{H}_4$ in Ne ($E_i = 0.10$ eV) and in He ($E_i = 0.36$ eV) at $T = 145$ K. The coverage indicates the total uptake on the surface.

Figure 4. Temperature dependence of the initial sticking probability, $S_0$, for ethene impinging at normal incidence on the clean Cu(410) surface.

Figure 5. Ethene uptake curves obtained from the data of Figure 1. The highest coverage reached corresponds to the total uptake, $\Theta$, while the asymptotic value after the flag intercepts the beam again corresponds to the stable coverage.
4. Discussion

Since, as demonstrated in the accompanying paper, no dissociation is found when ethene is dosed at room temperature, independently of the kinetic energy in the gas phase, we have to conclude that (a) also the activated dissociative process is mediated by an intrinsic precursor from which the molecules can either desorb or dissociate with a $T$ dependent branching ratio and (b) the barrier for desorption must be higher than the one for dissociation but the prefactor for dissociation must be much smaller than the one for desorption.

The potential energy surface for ethene/Cu(410) must therefore present a multiple adsorption well corresponding to the different sites available at the terraces and at the step. A consistent interpretation of the findings reported in this and in the accompanying paper implies the existence of five different adsorption states: two $\pi$ bonded ones ($\pi_0$ at the terraces and $\pi_1$ at the step edge), one fully dehydrogenated state (C≡C), one $\sigma$-bonded, and a metastable state [long bridge (LB) at the step edge], acting as a precursor for dissociation. These potential energy minima are interconnected by several paths. The details are illustrated schematically in Figure 7:

(1) $\pi_0$ and $\pi_1$ are $\pi$-bonded molecules at the terraces and at the step edges, respectively. $\pi_1$ is most reasonably on top of the undercoordinated step atoms in analogy to the case of ethene/Ag(n10)$^{18}$ and, according to DFT,$^{19,20}$ has a binding energy on the order of 0.52 eV. It is more stable than $\pi_0$, which again according to DFT has a bond energy of 0.30 eV.$^{20}$ These numbers imply desorption of $\pi_0$ at around 100 K and of $\pi_1$ at 200 K. The latter value is in accord with the HREELS data reported in ref 8 for Cu(410) and in ref 19 for sputtered and Cu adisland-covered Cu(111), which show that ethene at steps is stable up to 190 K. The TDS for Cu(410)$^{8}$ does not show two well-defined desorption peaks corresponding to $\pi$-bonded molecules, but the asymmetry of the 100 K peak may be indicative of desorption around 200 K. $\pi_0$ is little or not populated in our molecular beam experiments, since they are performed by dosing at 123 K or higher. Both $\pi_0\gamma$ and $\pi_1\gamma$-sites may be reached from the gas phase via nonactivated paths.

(2) From $\pi_0$ the molecules may either desorb or move to the more strongly bound $\pi_1\gamma$- and $\sigma$-states. The barrier height to transform from $\pi_0$ to $\sigma$ must be slightly larger than the one for desorption out of $\pi_0$, since (a) in TDS we always observe desorption out of the $\sigma$-state which is therefore always populated and (b) as shown by the HREELS experiments there is some dependence on the heating rate for the population of the $\sigma$-bonded state.

(3) The location of the $\sigma$-molecules at the surface cannot be determined from our data, but this state must be associated with the presence of a nanosized staircase with open step edges, since it forms neither when dosing ethene on low Miller index surfaces...
so that all molecules desorb once this process becomes possible.

at 300 K the prefactor for dehydrogenation must be very small
one for dissociation, while to explain the absence of dissociation
the He seeded beam at room temperature). To explain the low
molecules reaching LB dissociate, while at room temperature
rates. The barrier for dissociation must therefore be larger than
Dissociation dominates at high heating rates, desorption at low
From the values determined from TDS analysis we have to
demonstrated by TDS. The latter allows estimation of the barrier
for the barrier for dissociation is 0.65 eV with a prefactor of 109 s
-1. The low value of the prefactor implies that desorption occurs through an unlikely
pathway (e.g., if it is mediated by defects). The TDS estimate for the barrier for dissociation is 0.65 ± 0.03 eV with a prefactor of 5 × 1011 s
-1. The σ-state is populated efficiently when dosing at low T, as in our TDS experiments, implying that it is precursor-mediated by π, which is populated only at low T. From the values determined from TDS analysis we have to conclude that the di-σ-state is less strongly bound than π (though more than π).

(4) Molecules in π may either desorb or dehydrogenate. Dissociation dominates at high heating rates, desorption at low rates. The barrier for dissociation must therefore be larger than the one for desorption out of π.

(5) Dehydrogenation must occur through a precursor LB, which can be reached either indirectly through π or from σ to π (desorption route) are taken from the TPD analysis reported in ref 8.

nor on sputtered Cu(111). Possibly they may occupy bridge sites, as suggested in a theoretical paper on ethene/Cu(111). The latter case corresponds to adsorption at closed packed islands with reasonably close-packed step edges. From the σ-state the molecules can either desorb or dissociate as demonstrated by TDS. The latter allows estimation of the barrier for desorption out of the σ-state which comes out to be 0.466 ± 0.004 eV with a prefactor of 109 s
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(6) Conversion from π to σ is very unlikely in accord with the fact that the di-σ-state is less strongly bound. The dissociation of the di-σ-bonded molecules could, however, occur through π and LB (otherwise, we would still have another path for dissociation, which is unlikely since no dissociation is observed in absence of open steps). The barrier determined by TDS corresponds therefore to the barrier from π to LB rather than from σ to CC. This implies that conversion from σ to π is easy and does not limit the process.

Coming back to the sticking probability data, the increase of S with exposure might be accounted quantitatively by adsorbate-assisted adsorption given an increase of 0.2 at 0.2 ML coverage at 0.36 eV (see Figures 5 and 6). The effect is, however, absent for the carbon-contaminated surface, although C2 and C2H4 have very similar masses. The adsorbate-assisted mechanism should therefore be operative in both cases, contrary to experimental evidence. A consistent picture can however be achieved by invoking a pivotal role of the corrugation of the gas-surface potential:17 the increase of S with ethene coverage for the pristine surface is then due to an increase in the corrugation in the presence of adsorbed ethene, while C2 contributes less to corrugation sitting closer to the surface.

The initial sticking probability is larger for the carbon-contaminated surface than for the bare surface at θ = 45°, but it is the same at θ = −60°. This information indicates that, at θ = 45°, incoming ethene feels the corrugation associated to the presence of C2, while this is not the case at −60°. Carbon must therefore be at sites which cannot be easily reached by the latter molecules. The hollow site between the kink atoms at the step rises would fulfill this requirement, being in the shadow at the latter angle.

Careful inspection of the data shows that at the onset of adsorption, the sticking probability is slightly higher for molecules impinging at +45° than at −60°. In a reverse manner, the apparent saturation coverage is higher for −60° than for +45°. The latter difference is close to the experimental error for 0.36 eV [see also the S(θ) curves in Figure 3] but definitively larger for Ei = 0.10 eV. These results imply that the incoming molecules keep the memory of the direction they had in the gas phase and have therefore a different probability to hit against the step edge depending on whether they arrive step up or step down. For ethene colliding against the bare surface, it is thus easier to get rid of its energy when in the subsequent hits it collides with the Cu atoms building up the step rise, thus resulting in a higher sticking probability. For ethene colliding on the ethene-precovered surface, the situation is different, since its kinetic energy can be lost more efficiently when probing the larger corrugation produced by the preadsorbed companions, which sit at the upper side of the step edge when π-bonded. At θ ∼ 0.2 ML, the sticking probability is thus larger for molecules arriving step down, since they move in the right direction. The energy dependence of the process...
implies that, after the collision with the ethene precovered surface, slow impinging molecules find a site where they can chemisorb, while the fast ones have still a significant chance to be backscattered into the gas phase.

The above-reported experiments allow us to rationalize the very little angle dependence in the sticking probability. Indeed, at low $E_i$ the incoming molecules are unable to overcome the dissociation barrier and are then sensitive to the chemisorption well for $\pi$ (or at most for $\sigma$-$\sigma$) bonding. The ratio between $E_i$ and the potential energy well is low enough to remove the memory of the angle of incidence. At high $E_i$, the $\text{C}_2\text{H}_4$/Cu(410) system is characterized by the possibility of dissociative ethene adsorption, which implies a deep chemisorption well. The latter system is characterized by the possibility of dissociative ethene adsorption, which implies a deep chemisorption well. The latter process occurs via an intrinsic precursor.

The initial sticking probability is comparable for thermal and hyperthermal energies and nearly independent of the angle of incidence. The latter process occurs via an intrinsic precursor.

5. Conclusions

Ethene uptake on Cu(410) has been studied by means of a molecular beam at different angles and energies of impingement. Molecular adsorption is precursor-mediated and nonactivated. The initial sticking probability is comparable for thermal and hyperthermal energies and nearly independent of the angle of incidence. The latter process occurs via an intrinsic precursor.

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References and Notes

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