Employing a cylindrical single crystal in gas-surface dynamics

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We describe the use of a polished, hollow cylindrical nickel single crystal to study effects of step edges on adsorption and desorption of gas phase molecules. The crystal is held in an ultra-high vacuum apparatus by a crystal holder that provides axial rotation about a [100] direction, and a crystal temperature range of 89 to 1100 K. A microchannel plate-based low energy electron diffraction/retarding field Auger electron spectrometer (AES) apparatus identifies surface structures present on the outer surface of the cylinder, while a separate double pass cylindrical mirror analyzer AES verifies surface cleanliness. A supersonic molecular beam, skimmed by a rectangular slot, impinges molecules on a narrow longitudinal strip of the surface. Here, we use the King and Wells technique to demonstrate how surface structure influences the dissociation probability of deuterium at various kinetic energies. Finally, we introduce spatially-resolved temperature programmed desorption from areas exposed to the supersonic molecular beam to show how surface structures influence desorption features. © 2012 American Institute of Physics.

I. INTRODUCTION

The pioneering work by Somorjai’s group on the reactivity of small molecules on stepped platinum surfaces in the 1970s1,2 sparked a growing interest in the dependence of chemical reactivity on surface structure. A recent review by Rocca and co-workers summarizes part of the large body of research that has contributed to our understanding of differences observed in the chemistry occurring on low and high Miller index surfaces.3

A consideration in research that systematically compares reactivity on various vicinal surfaces, is the need for a series of single crystals with large areas of uniform surface structure. Recently, our laboratory has employed individual Pt single crystals exposing vicinal surfaces. These single crystals were cut from a single Pt boule to ensure the same impurity levels. We employed them in investigations of dissociative adsorption of H2 (Refs. 4 and 5) and coadsorption of H2O with 2H (Refs. 6 and 7) and 18O.3 In our experience, the amount of time required to perform such systematic studies scales almost linearly with the number of single crystals required to identify trends.

An interesting approach that may allow for much increased throughput is to employ monolithic single crystals with curved surfaces. Partially curved crystals were used first (see, e.g., Refs. 9–11) in the 1970s. In the following decade, the groups of Bauer12,13 and Woodruff14–17 explored the use of metallic cylindrical single crystals in surface chemistry and physics, while Ranke used cylindrical crystals of GaAs (Ref. 18) and Si.19 For a cylindrical crystal, the low Miller index surface structures are repeated at least twice along the circumference with, in principle, a gradual sequence of high Miller index surfaces in between. For example, Bauer’s group used a W cylindrical single crystal with the axis chosen in the [110] direction.12 Figure 1 shows a top view schematic of a fcc cylindrical single crystal, with the expected location of some vicinal surfaces (in the absence of step bunching and surface roughening). The (111) surface appears at four different locations, while (100) and (110) surfaces occur twice—at angles from the (111) planes of 54.7° and 35.3°, respectively. Ertl and Imbihl used a Pt cylindrical single crystal with its axis along a [100] direction.18,20,21 This choice leads to alternating (100) and (110) surfaces at 45° relative to each other, and various stepped surfaces in between.

The different groups that employed cylindrical single crystals also applied different surface sensitive techniques. Bauer’s group is, to the best of our knowledge, the only to publish low energy electron diffraction (LEED) images from the outer surface of a metallic cylindrical single crystal.12 Their images indicate that at least some vicinal surfaces were clearly identifiable. Ertl and Imbihl describe their LEED observations and indicate that visible faceting occurs on some areas of the surface.21 Bauer’s group also studied work function changes along the edge of their W cylindrical single crystal.12 Woodruff’s group investigated the related electron absorption and scattering from the circumference of Ni (Ref. 14) and Cu (Ref. 23) cylindrical crystals using Auger electron spectrometry (AES). They also investigated the rate of oxidation of both Ni (Ref. 14) and Cu,15 the adsorption
of various molecules by background dosing,\textsuperscript{15,16} and the oxidation of CO and \textsuperscript{13}H\textsubscript{2} by pre-adsorbed oxygen on Cu.\textsuperscript{17} Ertl and Imbihl employed their Pt cylindrical single crystal in the 1990s for photo electron emission microscopy (PEEM) studies of oscillatory reactions involving CO.\textsuperscript{20–22,24} In this paper, we describe our combined use of supersonic molecular beam techniques, high spatial resolution LEED, and spatially-resolved temperature programmed desorption (SR-TPD) with a nickel cylindrical single crystal. We show that this combination of techniques enables us to quantify step effects in gas-surface reaction dynamics, and we present an exemplary limited set of data on D\textsubscript{2} dissociation on (111) terraces of various width, separated by (100) steps. A larger set of data will be analyzed in detail elsewhere. To the best of our knowledge, this paper presents the first use of a cylindrical crystal in gas-surface dynamics studies.

\section*{II. EXPERIMENTAL}

Figure 2(a) presents a schematic of the nickel cylindrical single crystal and the sample holder designed for our studies (van der Veen Instrumentmakerij, Broek in Waterland, The Netherlands). Figure 2(b) shows a photograph taken of the assembled parts at the end of the horizontal X, Y, Z, \textgreek{\theta} sample manipulator (h). The cylindrical crystal (b) is spark eroded along the [110] direction from a high purity (5N low carbon) nickel single crystal rod, grown in a [111] direction and polished to a smooth finish on a specially designed polishing apparatus (Surface Preparation Laboratory, Zaandam, The Netherlands). The cylinder has an outer diameter of 20 mm, an inner diameter of 16 mm, and a length of 14 mm. A groove is spark eroded on the inside of the cylinder at $\sim$1 mm from the bottom face, providing a means to firmly attach the crystal to the sample holder without damaging the polished outer surface. The crystal is attached to a square oxygen-free copper cooling block (d), separated by three square plates (c). Two screws at opposite sides in the center plate push and pull two single crystalline nickel slides that can move in slots cut in the top two plates. The slides have edges that stick out above the top square plate and fall into the inner groove of the cylindrical crystal. The top plate is in contact with the cylindrical crystal and is made of pure nickel. The middle square plate is made from nickel-plated oxygen-free copper to provide good thermal conductivity. The lower plate is cut from an aluminium nitride slab and provides electrical isolation with good thermal conductivity. A filament (a) taken from a 150 W miniature light bulb (Osram, halogen display/optic lamp) is attached to electrically isolated tungsten rods protruding from the copper cooling block and square plates on the inside of the cylindrical crystal. An electrically isolated chromel-alumel thermocouple (i) also protrudes through the copper block and square plates on the inside and is attached to the cylindrical crystal’s outer edge. A 0.125 mm diameter W wire is also spot welded to the outer edge and is bent such that it sticks out and is aligned with the outer surface of the cylindrical crystal, serving as an antenna (not shown in Figure 2). The cylindrical crystal and sample holder have been designed such that the crystal’s rotational axis is also the rotational axis of the X, Y, Z, \textgreek{\theta} sample manipulator. The cooling lines (e) are only visible in the schematic. A holder for them (f) provides additional stability to the sample holder. Electrical and thermocouple wires are connected with the help of a ceramic plate (g) which electrically isolates all connections to the crystal from each other while keeping them in place.

The cylindrical single crystal can be heated radiatively and by electron bombardment. Electron bombardment allows for rapid heating to at least 1100 K by biasing the single crystal up to 250 V. Radiative heating is used for temperature programmed desorption experiments at 1 K/s. Flowing liquid nitrogen through the cooling block allows for cooling of the single crystal to 89 K as measured with a PID.
controller (Eurotherm, Series 900) with an external ice point reference. Cooling from annealing temperatures to 400 K is reasonably fast, averaging approximately 45 K/min. Cooling to well below room temperature is considerably slower. The lowest temperature is only reached approximately one hour after the final annealing step of cleaning procedures. We point out that the design of the crystal holder is not adequate for work that requires very low crystal temperatures. Cooling rates may likely be improved, e.g., by reducing the thickness of the three square plates separating the crystal from the copper cooling block. However, they may also induce larger temperature differences along the length of the cylindrical crystal and increase thermal stress when cycling the crystal temperature. Other possibilities would be cooling by liquid helium instead of liquid nitrogen or designing a sample holder that allows for cooling from both ends of the crystal. As our experiments for gas-surface dynamics studies require surface temperatures at or above room temperature, we emphasize that the current cooling rates are adequate for our purposes.

Figure 3 shows a schematic of the ultra-high vacuum (UHV)-supersonic molecular beam apparatus that houses the cylindrical crystal. Detailed information on the set-up of the supersonic molecular beam source and vacuum chamber can be found in Ref. 25. A supersonic molecular beam is created by 1–4 bar expansion of pure gases or gas mixtures from one of three simultaneously available nozzles with a 0.49 mm diameter nickel skimmer. Here, we use a 60 μm W nozzle. This nozzle can be heated radiatively and with electron bombardment up to 1900 K, although we generally do not exceed 1300 K. The molecular beam passes through two stages of differential pumping separated by a second skimmer with a circular 1.3 mm diameter orifice. The differential pumping stages house a beam flag, a high-speed chopper wheel for time of flight (TOF) measurements, and a push-pull gate valve. The beam enters the UHV chamber through a rectangular slot. We have used two different rectangular slots that skim the beam to a size of either 1.0 mm × 5.2 mm or 0.4 mm × 5.2 mm at the cylindrical crystal position. The beam encompasses a 6° or 2° angle of the 360° circumference when impinging onto the crystal surface depending on the slot used. All data presented in this paper were obtained using the narrower of the two slots between the UHV and second differential pumping stage.

When the crystal is retracted, the molecular beam enters the ionization area of a differentially pumped quadrupole mass spectrometer (QMS; a linear version of a Baltzers QME 421) through a second rectangular skimmer of 1.0 mm × 6 mm. The QMS can be retracted up to 175 mm along the molecular beam path for TOF measurements. With the crystal in dosing position, the differentially pumped QMS may also be used for SR-TPD. We align the surface area exposed to the supersonic molecular beam with the rectangular opening of the QMS chamber by rotation of the crystal over 180°. A moveable inert flag is positioned in the UHV chamber such that it may block the supersonic molecular beam from impinging onto the cylindrical crystal’s surface. Its shape is chosen so that it does not reflect the molecular beam toward our second and third QMSs (Baltzers QMA 430 and Prisma). Both QMSs are positioned far away from the molecular beam and are not in line with any (near-)specular reflections of the beam from any internal surface. This ensures that it can be used for accurate King and Wells measurements26 to determine absolute reactivity.

At a different position along the manipulator’s axis, a microchannel plate-based four-grid LEED (OCI Vacuum Micro-engineering) determines surface structure along the crystal’s outer surface. The electron beam diameter is 0.43 mm when using an electron beam current of 30 nA. The electron beam diameter at the crystal surface was determined by deconvolution of the measured current to the “antenna” (see beginning of this section) as a function of height relative to the electron beam axis. LEED measurements encompass 2.46° of the 360° circumference of the cylindrical crystal. The beam diameter was not determined for the AES mode as we routinely employ a separate double-pass cylindrical mirror analyzer (CMA) for AES measurements. The electron beam diameter of this CMA is estimated to be in the range of 0.5 to 1 mm and therefore provides a signal from a larger surface area.

We use a single cleaning procedure for the whole circumference of the cylindrical Ni single crystal. Our recipe is based on methods commonly used to clean low Miller index surfaces (see, e.g., Refs. 27–30). Sputtering is performed using Ar+ at 0.8 kV, resulting in a sputtering current of 5–6 μA at the crystal. During sputtering the sample is rotated in steps of 10° every 10–15 minutes. We anneal the crystal at temperatures between 900 and 930 K while dosing oxygen (2 × 10⁻⁸ mbar, 30 s) and hydrogen (1 × 10⁻⁶ mbar, 3 min.) through leak valves to remove carbon, especially at or near the (100) face. Then the crystal is kept in the same temperature range for another 3 minutes. After repeated sputtering and annealing cycles, we use AES to verify surface cleanliness. We note that the size of the electron beam for AES measurements does not allow us to probe a (111) face exclusively. At this point of reference, the electron beam encompasses vicinal surfaces with (111) terrace widths ≥18 atoms separated by (100) or (110) steps. The presence of these steps would introduce a minor ambiguity in the actual surface coverages for
any adsorbate, even when establishing the AES signal intensity for a defined surface coverage as reference.

III. RESULTS AND DISCUSSION

A. Auger electron spectroscopy

Figure 4(a) shows an example of an AES spectrum taken at an exemplary part of the surface after cleaning. The characteristic Ni peaks at 61, 716, 783, and 848 eV are evident, while the common contaminants S (152 eV) and C (272 eV) are absent. Two additional peaks around 135 and 200 eV are not representative of any known contaminant. We observe these peaks in all spectra, with intensities depending on the surface structure and sample temperature. The exact position of the peaks shifts with surface orientation; the peaks are also influenced by settings of the electron gun. The Ni peaks (or C, O, or S when present) show no such sensitivity. We conclude that the broad features at 135 and 200 eV are likely caused by diffraction.

For the determination of absolute coverages using Ni as an internal reference, it is important to realize that Auger intensities vary with surface structure. This dependence is related to the inverse Kikuchi effect. The Kikuchi effect is a scattering effect. Electrons get scattered multiple times without losing significant amounts of their incidence energy.31 The term inverse Kikuchi effect is used for the electrons that can get scattered multiple times but then get absorbed. This can be demonstrated by measuring the sample current collected from a constant electron flux as a function of rotational angle of the cylindrical crystal.23 Figure 4(b) shows the dependence of sample current on the rotational angle of the sample. The general shape of the curves obtained during separate experiments (not shown) matches very well with the exemplary one. Different amplitudes of the signal are caused by different settings for the focus of the AES spectrometer. Once the surface structure at certain angles has been determined, and the curve in Figure 4(b) has been measured, these data can be used to determine the orientation of the sample within the experimental chamber. Very similar trends are observed for elemental peaks (not shown here). As a consequence, no detection limits for adsorbates were established. A separate quantification for every single type of surface structure would be necessary due to different signal intensities and most likely different maximum coverages. Our results differ from those reported by Woodruff et al.14 That is due to the fact that the inverse Kikuchi effect is very sensitive to the geometrical arrangement of the experiment. Ours works with a 90° angle of incidence for the electron beam and a solid detection angle of 6% 2π sr for the AES; theirs had an angle of incidence of 15° with detection at a 42° polar angle to the crystal surface and ±60° of azimuthal angle.14

B. Low energy electron diffraction

Figure 5 shows four LEED images taken at approximately 100 K after cleaning an area of 80° that encompasses a (100) and a (111) face. All LEED pictures in Figure 5 were obtained with electron beam energies between 152 eV and 161 eV. We have observed all four (111) faces to within 1° of the appropriate angles relative to the (100) face, as well as two (110) faces. With the crystal mounted at a different orientation, we have previously observed the two (110) faces, a single (100) face, and four (111) faces, all at appropriate angles relative to each other. The last (100) face was not accessible, as part of the crystal holder comes into contact with the LEED’s cylindrical μ-metal shield. LEED images have also been taken along the length of the cylindrical crystal. We observe no deviations from those shown in Figure 5 over the accessible length of the cylindrical crystal (~10 mm). Our LEED observations confirm that the nickel cylinder contains no glide planes or other defects that reorient the direction of
the low Miller surfaces throughout the diameter and over the length of the single crystal, as previously documented by Laue x-ray back reflection (Surface Preparation Laboratory, Zaan- dam, The Netherlands).

Figure 5(a) shows a LEED image of a (111) surface of the cylindrical Ni crystal. We observe sharp spots. In Figure 5(b) the sample was rotated by 4° away from the (111) surface towards the next (100) surface. No spot splitting can be seen yet, but the spots characteristic of (111) terraces are visibly elongated. Upon further rotation spot splitting becomes clearly visible. Examples are Figures 5(c) and 5(d), where the sample is rotated relative to the (111) surface by 6° and 11°, respectively. In Figures 5(c) and 5(d), we also observe weakly curved lines connecting the split spots. On conventional stepped surfaces straight lines and streaking have been reported.32 We expect that the macroscopic shape of the crystal is responsible for the curvature, which complicates the analysis of LEED patterns compared to flat vicinal surfaces.33, 34 Nevertheless, spot splitting occurs gradually and LEED patterns change smoothly when moving away from (111) and (100). There are no indications of surface roughing or step bunching. Therefore, in the regions near the low Miller-index surfaces, we find that surface structures change smoothly and we can predict surface structure at specific angles relative to the principal surfaces (e.g., Table I). In the region where we expect the change from (111) to (100)

![LEED patterns](image)

**TABLE I.** Overview of expected surface structures at specific surfaces of the crystal.

<table>
<thead>
<tr>
<th>Rotation off (111) surface</th>
<th>Predicted (111) terrace length</th>
<th>$S_0$ ($E_{kin} = 0.8$ kJ/mol)</th>
<th>$S_0$ ($E_{kin} = 10.0$ kJ/mol)</th>
<th>$S_0$ ($E_{kin} = 23.6$ kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>infinite</td>
<td>0.07</td>
<td>0.12</td>
<td>0.67</td>
</tr>
<tr>
<td>4</td>
<td>14</td>
<td>0.23</td>
<td>0.12</td>
<td>0.46</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>0.30</td>
<td>0.14</td>
<td>0.54</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>0.47</td>
<td>0.19</td>
<td>0.50</td>
</tr>
</tbody>
</table>
terraces additional complexities are observed that are still under investigation.

C. Dissociative adsorption from a supersonic molecular beam

We have determined the absolute probability of dissociative D$_2$ adsorption, as a function of crystal rotation at three different kinetic energies of incidence. To this end we utilized a supersonic molecular beam of D$_2$ (pure or seeded in Ar), with a stagnation pressure of 2.5 bar, and nozzle temperatures of 300 K or 1300 K in a King and Wells experiment.$^{26}$ During this experiment, the D$_2$ beam is introduced stepwise into the chamber. First the effusive load is let into the reaction chamber and produces a small background. Then the first flag is opened and the supersonic molecular beam is allowed into the reaction chamber, where it does not yet hit the sample. Thus the pressure increases. Subsequently the second flag is opened and the sample is exposed to the incoming D$_2$ molecules. A fraction of them dissociatively adsorbs, causing a drop in pressure. The ratio of the drop in partial pressure upon removing the last flag to the increase when opening the first flag provides the absolute reaction probability in the zero-coverage limit, $S_0^hkl$. Figures 6(a)–6(c) show typical King and Wells traces for the supersonic molecular beam impinging onto the surface when rotated 0°, 4°, 6°, and 11° away from the (111) surface, with the three different kinetic energies. TOF measurements indicate that the kinetic energy of deuterium was 0.8 kJ/mol, 10.0 kJ/mol, and 23.6 kJ/mol.

FIG. 6. King and Wells traces for D$_2$ dissociation with a kinetic energy of (a) 0.8 kJ/mol, (b) 10.0 kJ/mol, and (c) 23.6 kJ/mol on a (111) surface and several stepped surfaces of the cylindrical sample. (d) A plot of the sticking coefficient dependence on the surface coverage ($S_0^hkl$) for the trace with the highest reaction probability from (a).
We compare our results of Figure 6 to those obtained with different techniques using flat single crystals. For Ni(111), dissociation probabilities of below 0.01 to for H₂ and D₂ have been observed by various groups employing different methods at kinetic energies of roughly 1 kJ/mol. We observe an initial reaction probability of 0.07. As we impinge D₂ over a 2° angle, the assumption of working on a “perfect” (111) surface does not hold even though the LEED pattern shows no spot splitting. Therefore it seems likely that the small density of steps increases the reactivity. Nevertheless this does not entirely account for higher reactivity. For stepped nickel surfaces, published results for hydrogen adsorption dynamics are scarce. On a Ni(977) crystal an initial reaction probability of 0.24 for a bare surface was determined by Winkler et al. For a Ni(997) surface an initial sticking coefficient of 0.19 was observed. Both studies were performed employing thermal beams instead of supersonic expansions.

The King and Wells traces of the stepped surfaces we show here are obtained upon the rotation of the crystal in front of the molecular beam by 4°, 6°, and 11° relative to the (111) surface. Calculations predict surfaces with average (111)-terrace widths of 14, 9, and 5 atoms, respectively. In all cases the step orientation is (100). Results are compiled in Table I. Within a row the change of initial dissociation probability for one surface with D₂ beams of different kinetic energies can be seen. In the columns, the reactivities of the different surfaces at the same kinetic energy of D₂ can be compared. We observe that the initial reaction probability at extremely low kinetic energy of D₂ increases significantly when steps are introduced. At higher kinetic energy of 10 kJ/mol the initial dissociation probability decreases significantly for all stepped surfaces investigated here, while at the (111) surface the reactivity increases. At even higher kinetic energies of more than 20 kJ/mol the reactivity for all surfaces increases again. The highest reactivity occurs at the (111) surface. This is in agreement with our expectations according to previous results obtained on different surfaces of Pt (for example by Groot et al.) and theory.

McCormack et al. observed a non-activated precursor-mediated reaction channel due to molecular chemisorption wells for H₂ at the bottom of the step-terrace border in their calculations for the Pt(211) surface. This channel is responsible for the drop of initial dissociation probability with increasing kinetic energy of the hydrogen. Further they found an activated direct dissociation pathway on the terrace atom. With increasing kinetic energy this channel gains importance. As a third channel they observed direct non-activated dissociation at the step edge atoms.

Our measurements show the same behavior for D₂ dissociating on stepped Ni surfaces. This strongly indicates a precursor mediated adsorption process on stepped Ni surfaces with (111) terraces and (100) step edges.

Note in Figure 6(a) that, at low kinetic energies, our D₂ flux is low enough that reactivity only gradually decreases over extended periods of time. Although we do not focus on it here, these data allow us also to extract the coverage dependence of the dissociation probability at any surface structure, S_{θ, hkl}. An example of that is given in Figure 6(d). In this graph, it can also be seen that the reaction probability is decaying monotonously, as expected, but three different sections are observed: at the very beginning the initial dissociation probability stays nearly constant over a short coverage regime. Then a steeper linear decay is observed. Finally, a sharp transition to a less steep part is observed. This behaviour is not in agreement with Langmuir-type adsorption.

We conclude that our cylindrical single crystal allows us to study the influence of step density on the dynamics of dissociative adsorption onto a large range of surface structures using only one single crystal.

D. Temperature programmed desorption

Figure 7(a) shows SR-TPD features for m/e = 4 after impinging D₂ from the molecular beam onto a surface close to (111) and a series of nearby surfaces for extended periods of time. In this series the dosing — and accordingly the TPD angle — were changed in 2° steps. The experiment shows that we indeed obtain an experimental resolution of 2°. In the series of TPD traces in Figure 7(a), we observe that the TPD experiment is very sensitive to surface structure. A small rotation strongly affects the desorption temperature and peak shape as indicated by a straight line. The first spectrum corresponds to a surface close to the (111) surface and shows the typical double peak structure. Upon rotation the first of the two peaks

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**FIG. 7.** (a) Different TPD traces recorded from the cylindrical single crystal recorded at different angles, subsequently rotated by 2°. (b) Comparison of TPD traces obtained from a (111) Ni single crystal (black) and a (111) area of the cylindrical single crystal (grey).
decreases in intensity while the second peak becomes more intense and shifts to higher desorption temperatures. These results indicate that the binding energy of D at the (100) step edge atoms is higher than that of D on (111) terrace atoms.

We compare the SR-TPD results to previous studies of hydrogen desorption from flat nickel surfaces. In Figure 7(b), a TPD trace recorded in our lab from a “standard” Ni(111) crystal (black) is compared to a TPD trace taken from a (111) region of our cylindrical sample (grey). The shape and width of the spectra match extremely well. To overlap the two traces the temperature scale of the experiment from the “standard” Ni(111) crystal had to be corrected by approximately 10 K.

We conclude that our cylindrical single crystal allows us to study desorption from particular surface structures without significant interference from the curvature of the crystal.

E. Conclusions

In this study we have shown that cylindrical single crystals can be used for spatially resolved molecular dynamics studies in adsorption as well as desorption measurements. Results compare well to those obtained from “flat” single crystals. Molecular dynamics measurements are not influenced by the macroscopic shape of the sample and several different surfaces are accessible within a short period of time. At the same time it is certain that impurities in the material, as well as sample preparation and experimental procedures, are identical for all surfaces. The primary disadvantage in this type of experiment stems from the huge mass of the crystal and correspondingly long heating and cooling times. This can hamper measurements for which a low surface temperature and a correspondingly long heating and cooling times. This can hamper measurements for which a low surface temperature and a clean surface are needed. Determination of surface structure is more difficult compared to “flat” single crystals. Nevertheless it is possible to demonstrate that the surface structure of the cylindrical surfaces changes smoothly and no step bunching occurs — at least in areas with low step densities.

The results of the King and Wells measurements indicate that on stepped Ni surfaces with (111) terraces and (100) step edges the same dissociation pathways are accessible as on Pt-surfaces with comparable structure.

The spatially resolved TPD experiments show that these experiments are highly sensitive to surface structure and that $D_{\text{ab}}$ binds more strongly to the (100) step sites than the (111) terrace sites.

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