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Frozen thermal fluctuations in adsorbate-induced step restructuring

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Ammonia adsorbed on a Pt(443) surface causes meandering of the initially straight edges at 300 K. Based on density-functional theory calculations and on kinetic Monte Carlo simulations it is shown that the meandering is not an equilibrium structure stabilized by the larger adsorption energy of ammonia at step and kink sites. Rather the meandering has to be interpreted as a frozen thermal fluctuation caused by ammonia which strongly reduces the stiffness of the step edges at intermediate ammonia coverages.

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Surfaces are typically modified by catalytic reactions often leading to real morphological changes.^{1,2} A well-known example is the oxidation of ammonia with air in the so-called Ostwald process where the Pt/Rh gauze becomes visibly roughened already during the first minutes of operation.³⁻⁵ As a model system for such a restructuring process we can consider a stepped metal surface because any restructuring will have to start with a change in the step structure. Due to their reduced coordination number step atoms often exhibit an enhanced catalytic activity.⁶ On a clean-surface atomic steps display interesting dynamics, because a straight step edge may fluctuate causing step atoms to move temporarily away from their equilibrium position.⁷⁻⁹ The energetics of atomic steps and their orientational dependence were shown to be essential for an understanding of the morphology of epitaxially grown metal layers.¹⁰⁻¹²

There have been various studies dealing with the overall morphology of a surface with steps and how this morphology is affected by adsorbates.¹³⁻¹⁷ Here we report on the restructuring of a stepped platinum surface in the presence of adsorbed ammonia. We focus, however, on a single step and on the details of the meandering of such step. Supported by density-functional theory (DFT) calculations and kinetic Monte Carlo (kMC) simulations we show that the ammonia-induced meandering of an initially straight step edge has to be interpreted as a frozen thermal fluctuation. For the experiments we use a conventional UHV chamber equipped with a low-energy electron diffraction (LEED)/Auger system and a scanning tunneling microscope (STM) from DME. The DFT calculations were conducted with the VASP package^{18,19} and the kMC simulations with the Carlos program.²⁰

We have studied a Pt(443) surface, which in its clean state consists of monatomic (111) steps separated by seven lattice units wide (111) terrace [Fig. 1(a)] as demonstrated by the STM image in Fig. 1(b). When we expose this sample to ammonia at 300 K with $p_{\text{NH}_3} = 10^{-6}$ mbar we note that first individual Pt atoms move along the step edge as shown by Figs. 1(c) and 1(d). These atoms migrate and become again attached rigidly to the step edge. Thus holes and protrusions are formed along the step edges generating a meandering of the step edges as shown in Fig. 1(e). This meandering takes

place in about 10–15 min. The dynamics of the substrate changes are frozen in when after approximately 30 min an ordered (2×2) ammonia overlayer forms on the (111) terraces visible in the STM image in Fig. 1(f). In LEED the splitting of the integral order beams remains unchanged indicating that the average separation of the step edges is not altered by meandering. This result supports the interpretation suggested already by the STM images that mass transport of Pt occurs practically exclusively along step edges (intrastep diffusion) but not across step edges (interstep diffusion).

With the mass spectrometer we could not detect any product formation during the above adsorption experiment. This is in agreement with reports in the literature that at 300 K Pt surfaces are not active in ammonia decomposition.^{21,22} We can therefore exclude possible decomposition products $\text{NH}_{x,\text{ad}}$ ($x=0, 1, 2$) and H_{ad} as stabilizing factors for the restructured step edge. Clearly the driving force for restructuring has to be provided by molecularly adsorbed ammonia alone.

Several aspects of the energetics of meandering are obvious. The number of Pt-Pt bonds of the step atoms decreases when the step starts to meander thus increasing the step energy of the step. Simultaneously, due to bond-order conservation the remaining bonds of the Pt step atoms will become stronger, and the NH_3 adsorption energy is expected to be highest on Pt step and kink atoms.²³ A first guess would therefore be that the meandering is driven by the gain in ammonia adsorption energy caused by creation of low coordinated sites. To check this explanation plane-wave DFT calculations were performed.²⁴ First, the energy costs for restructuring were determined by calculating Pt slabs without ammonia with 19 different structures.²⁵ The structures varied in the thickness of the slab, type of step, width of the terrace, and density of the kinks. The energies of these structures were then modeled by $\Delta E = N_{(100)}E_{(100)} + N_{\text{kink}}E_{\text{kink}} + N_{\text{lone}}E_{\text{lone}}$. In this expression ΔE is the energy difference between a meandering step and a straight (111) step with the same number of atoms. $N_{(100)}$, N_{kink} , and N_{lone} are the number of atoms at the step edge forming a (100) step, the number of kinks, and the number of lone atoms, respectively. These numbers correspond to the number of atoms of type B, C, and E, respectively, in Fig. 2. We do not need the number of

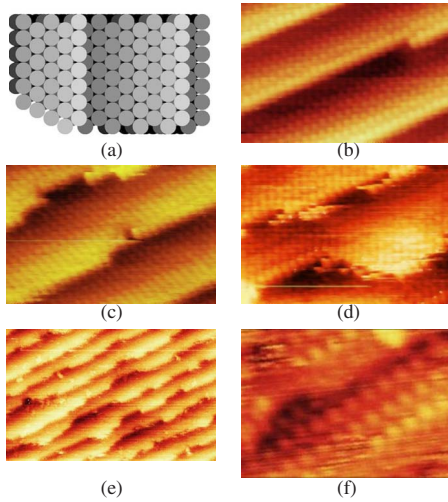


FIG. 1. (Color online) STM images showing the meandering of the step edges on a Pt(443) surface during exposure to ammonia at 300 K with $p_{\text{NH}_3}=10^{-6}$ mbar. $t=0$ refers to at the beginning of adsorption when the coverage is zero. (a) Structural model of Pt(443); (b) clean surface; (c) $t=3$ min; (d) $t=15$ min; and (e) $t=15$ min. The image in (f) at $t=35$ min, at maximum coverage displays formations of a 2×2 -NH₃ structure. Sizes of the imaged areas are (b)–(d) $50 \times 30 \text{ \AA}^2$, (e) $150 \times 95 \text{ \AA}^2$, and (f) $45 \times 30 \text{ \AA}^2$.

A atoms forming a (111) step because we use this step for our reference energy. The number of inside-corner atoms D is always equal to $N_{\text{kink}}+2N_{\text{lone}}$. We have found that $E_{(100)}=11$ kJ/mol, $E_{\text{kink}}=41$ kJ/mol, and $E_{\text{lone}}=41$ kJ/mol. Our results are in reasonable agreement with those of Boisvert *et al.*²⁶ and Feibelman,²⁷ although the latter finds a (100) step that is slightly more stable than the (111) step. However, our kink energy is larger than the experimental value.^{7,8} This is because experimentally the meandering is described by just one parameter, the kink energy, whereas our model has the kink energy and the energy to form a (100) step. The latter becomes important when the kink is more than one row of atoms deep. Because $E_{(100)} < E_{\text{kink}}$ the experimental kink energy will be lower than ours. One might expect that it should cost more to form a lone atom than to form a kink atom. But

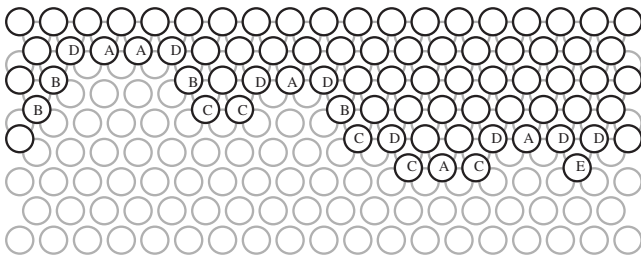


FIG. 2. Sketch of an arbitrary step configuration similar to the experiment which indicates the types of atoms that can be found at a step. There are (A) atoms forming a (111) step, (B) atoms forming a (100) step, (C) outside-corner atoms, (D) inside-corner atoms, (D) and lone atoms.

TABLE I. Adsorption energies (in kJ/mol) of NH₃ atop Pt atoms with different coordinations calculated using DFT (except for the last two entries). Pt(331) has the same step structure as Pt(443) but the unit cell is smaller because the terrace is narrower. The result for the inside-corner atom is taken as the average of the adsorption energies on Pt(111) and on the (111) step. The result for the lone atom is taken equal to the adsorption energy of the outside-corner atom as it costs the same energy to form such atom.

Pt surface	Site type	Adsorption energy
Pt(111)	Terrace	−68
Pt(331)	Terrace	−76
Pt(211)	(100) step	−90
Pt(331)	(111) step	−94
Pt(331)	Kink; outside corner	−111
	Kink; inside corner	−81
	Lone atom	−111

while each kink contains only one atom of type D, each lone atom of type E possesses two atoms of type D. This energy roughly compensates the smaller number of Pt-Pt bonds of the E atoms.

Ammonia adsorbs on top sites of the Pt surface. Table I shows DFT results for the adsorption energy of ammonia on Pt atoms with different coordination numbers. These energies include the interaction of ammonia with the substrate but also the induced weakening of the Pt-Pt bonds. We see a very pronounced increase in the adsorption energy as the coordination number of the Pt atom decreases. It turns out, however, that the effect is too small to compensate for the energy costs of meandering. The adsorption energy at a kink site is 17 kJ/mol larger than at a straight (111) step. This means that it will still cost $41-17=24$ kJ/mol to form the kink even when ammonia is present.

We should also take into account that the increase in the step length by meandering transforms ammonia on terrace sites into ammonia on step sites. For a kink or lone atom this yields 43 kJ/mol. The gain is smaller on inside-corner atoms. Simulations (see below) show that at 300 K the length of the step increases by about 13%, but the number of ammonia molecules at the step edge decreases by about 7%, because of the mismatch between the (2×2) structure and the shape of the step. The gain in adsorption energy never yields back more than 30% of the cost of meandering; on average even only 15%.

Due to reduced steric restrictions, in principle, more ammonia molecules can adsorb at a step compared to the density of ammonia in the (2×2) structure.²⁸ This extra stabilization of the step will, however, hardly provide the missing give 70% or more of the energy required to make meandering profitable.

The failure of a simple energy balance to explain the experimental findings motivated us to do kMC simulations. We modeled ammonia adsorption on a surface with a single step (with a length of 128 Pt atoms and periodic boundary conditions) allowing Pt atoms and ammonia molecules to diffuse on the upper and lower terraces but not across the step.²⁰ To account for the formation a (2×2) structure of ammonia at a

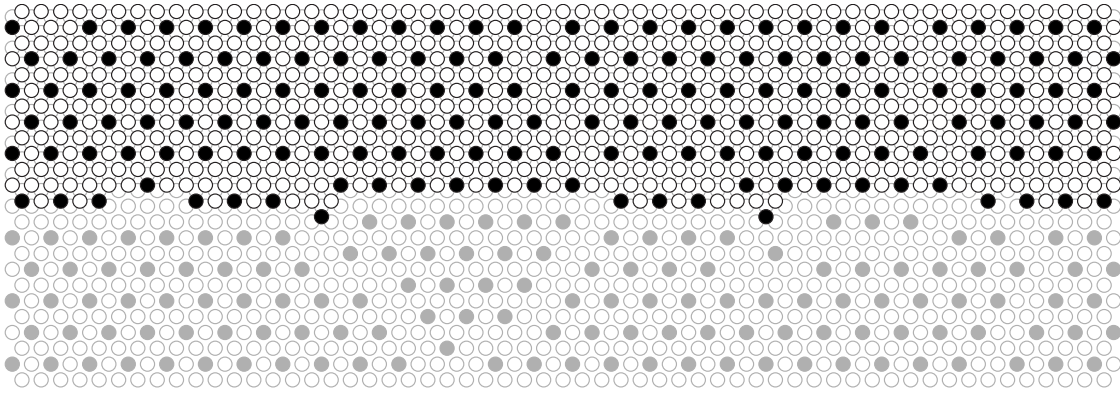


FIG. 3. Snapshot of a kMC simulation showing part of a step formed with NH_3 . Open circles are Pt atoms without NH_3 , closed circles are Pt atoms with NH_3 . The lower terrace is in a lighter shade.

$1/4$ ML coverage molecules are not allowed to become nearest or next-nearest neighbors. We have assumed that the minimum-distance restriction for two ammonia molecules also holds for ammonia on the lower terrace and Pt atoms forming the upper terrace. We tested reducing the minimum distance. This gave essentially the same results.

We have assumed that adsorption of ammonia is a simple direct adsorption. The rate constant of such process is given by $k_{\text{ads}} = p_{\text{NH}_3} A_{\text{site}} \sigma / \sqrt{2\pi m_{\text{NH}_3} k_B T}$ with A_{site} the area of an adsorption site and the sticking coefficient $\sigma=1$ for a vacant²⁹ and $\sigma=0$ for an occupied site. All diffusion is modeled by hops between neighboring sites. The rate constants of these hops are given by $\nu \exp[-E_{\text{act}}/k_B T]$. We do not have proper values for E_{act} . However, diffusion is fast and just brings the system to equilibrium between two adsorption events. We can model this by taking $E_{\text{act}} = \max(0, \Delta E)$ with ΔE the change in energy when a hop occurs. The prefactor is taken equal to $2 \times 10^7 \text{ s}^{-1}$, which is so large that an additional increase does not change the simulation results, and which proves that equilibrium is indeed obtained. The time scale in our simulations is determined by the adsorption rate and is the same as in the experiments.

The energies $E_{(100)}$, E_{kink} , and E_{lone} from the DFT calculations have been used to calculate how the energy changes when Pt atoms move without ammonia. The adsorption energies in Table I have been used to calculate energy changes for ammonia diffusion. Energies for diffusion of Pt in the presence of ammonia have been calculated by splitting the process in three steps. In the first step all ammonia is removed, in the second the Pt moves, and in the third ammonia is placed back at appropriate sites. The energies for the first and third steps can be calculated from the adsorption energy in Table I, the energies for the second step from $E_{(100)}$, E_{kink} , and E_{lone} . The changes in energy for Pt diffusion in the presence of ammonia are simply obtained by adding the energy changes in the three steps. This means that, except for the last two entries in Table I, our simulations are fully based on DFT results.

The kMC simulations without ammonia do not show any meandering at 300 K. This is not surprising as the energy changes are much higher than the thermal energy. Only when we increase the temperature in our simulations to around 600 K or higher we see deviations from the straight (111) step.

Starting with a bare surface we observe that during ammonia adsorption the initially straight (111) step starts meandering as the coverage of ammonia builds up. This is because part of the energy costs to form kinks is offset by the higher adsorption energy of ammonia at kink atoms. As a consequence there is a decrease in the stiffness $\tilde{\beta}$ of the step. We have determined the stiffness by fitting the mean-square wandering amplitude $\langle [y(x+\Delta x) - y(x)]^2 \rangle$ to $(k_B T / \tilde{\beta}) |\Delta x|$ for small Δx . Here $y(x)$ is the amplitude of the deviation from a straight (111) step at coordinate x along the step. The average is over x . Without ammonia we find $\tilde{\beta} = 0.251 \text{ eV}/\text{\AA}$ (at $T = 550 \text{ K}$), 0.204 (600 K), and 0.175 (650 K). Although there is quite some scatter in the experimental results, our values for the step without ammonia are in reasonable agreement with most of them.^{7-9,16} With ammonia we find $\tilde{\beta} = 0.251 \text{ eV}/\text{\AA}$ (at $T = 300 \text{ K}$), 0.032 (350 K), and 0.034 (400 K). There are no experimental results for the step with ammonia, but we see that there is a very large reduction in stiffness caused by ammonia.

As long as there are kink and lone Pt atoms without ammonia the shape of the step keeps changing. The meandering stops, however, almost completely when no more ammonia can be added to the step edge. At that point some Pt atoms at the step edge can still move, but each Pt hop is immediately followed by its reverse hop. The shape of the step is then fixed. More extensive changes to the step do not occur because they would now drive ammonia to less favorable adsorption sites and would involve structures with energies that are substantially higher than the thermal energy. If the coverage of ammonia is increased further, then also the remaining Pt hops at the step edge become suppressed. This is because the Pt atoms at the step become blocked by ammonia at the lower terrace. We find that it takes about 20 min to freeze the step when we use the experimental pressure of ammonia. This is in good agreement with the experimental results. Also the shape of the final step is in good agreement with the STM images (see Fig. 3).

So the behavior of the step based on the STM experiments and the kMC simulations can be summarized as follows. Without ammonia the straight (111) step is energetically the most favorable structure and hence the equilibrium structure. There are no fluctuations in the structure at $T = 300 \text{ K}$

because structural deviations from a straight edge have energies that are substantially higher than the thermal energy. Adding ammonia still leaves the structural deviations energetically unfavorable but the energy difference is now reduced strongly enough to allow for thermal fluctuations. This leads to meandering. When the density of ammonia at the step edge becomes high, the diffusion of Pt atoms is suppressed because any jump generates locally energetically unfavorable configurations because ammonia would be forced to unfavorable sites. The final structure of the step can therefore be regarded as a frozen thermal fluctuation. We have thus demonstrated that analyzing in detail the influence of adsorbates on the energetics and kinetics of substrate atoms is essential for a proper understanding of adsorbate-induced

restructuring. Note that our explanation does not depend on the precise details of the DFT calculations. At low coverage ammonia makes it easier for the step to start meandering because it creates more favorable adsorption sites. At high coverage the meandering stops because otherwise ammonia would be driven to less favorable adsorption sites.

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