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# Mechanism and Dynamics of the CO-Induced Lifting of the Pt(100) Surface Reconstruction

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The first atomistic simulations of the CO-induced lifting of the Pt(100)-hex reconstruction have been performed. During this phase transformation the surface changes back to bulk-terminated Pt(100)-(1 × 1), whereby the surface atom density decreases by ~20%. The simulations reveal a mechanism collective in nature, indicating that restructuring proceeds through ejection of chains of Pt atoms. These chains explain the anisotropy as seen in scanning tunneling microscopy experiments. The restructuring rate depends nonlinearly on the CO coverage, but the absence of local clustering of CO excludes an explanation in terms of elementary reaction kinetics as proposed previously.

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One of the most intensively studied systems in surface science is adsorption of CO on Pt(100), for reasons of fundamental as well as applied interest. The oxidation of CO on Pt(100) has a similar archetypal role in catalysis. Among its most interesting features is the oscillatory behavior of the reaction under certain conditions [1,2]. The reason for this behavior is related to the different reactivity of the two surface phases that Pt(100) exhibits, towards the reactants. The clean Pt(100) surface is reconstructed, exposing a quasihexagonal close-packed top layer (Fig. 1). This reconstruction, normally referred to as the hex phase, which undergoes a slight rotation of  $0.7^\circ$  above about 1100 K, reconstructs to the regular, bulk-terminated square (1 × 1) phase upon adsorption of CO, NO, and several other adsorbates. The hex surface plane contains 20% to 25% more Pt atoms than the square surface plane, and it is generally believed that these excess surface atoms are forced up during the surface deconstruction, to become adatoms, which can coalesce to form islands and steps. Our current understanding of the mechanism of this CO-induced hex → (1 × 1) phase transition is based on experimental data obtained by several research groups, using techniques including LEED, infrared spectroscopy, molecular beam, and scanning tunneling microscopy (STM). In this Letter, we show that a theoretical study can reproduce some of the finer details of these experiments and at the same time contribute to a deeper understanding of the atomistic driving forces of the process. The method we employ is a novel approach to adsorbate/surface systems, using a density functional theory (DFT) based parametrization of modified embedded-atom method potentials, enabling for the first time molecular dynamics (MD) simulations of the adsorbate-induced lifting of a surface reconstruction. These MD simulations reveal for CO/Pt(100)-hex a restructuring mechanism which is collective in nature.

The experimental studies mentioned above revealed that even at CO coverages below 0.1 monolayers (ML)

the phase transition occurs locally at temperatures around 300 to 500 K [4–6]. However, where it occurs, the local CO coverage on the resulting (1 × 1) patches is 0.5 ML [4,7]. When the overall CO coverage on a fully reconstructed surface drops below ~0.3 ML, the hex phase starts to reappear [4,8]. Further, it was concluded that the restructuring is heterogeneously nucleated at linear defects. Subsequent growth of the arisen (1 × 1) domains proceeds anisotropically, the preferred direction being  $[0\bar{1}1]$  (Ref. [9]), with a rate that depends in a highly nonlinear fashion on the local CO coverage [10].

On the theoretical side, when tackling this system one faces the problem of the large number of atoms involved, which makes DFT impossible at the present. A further complication is the fact that current DFT implementations are not able to reproduce the correct binding sites of

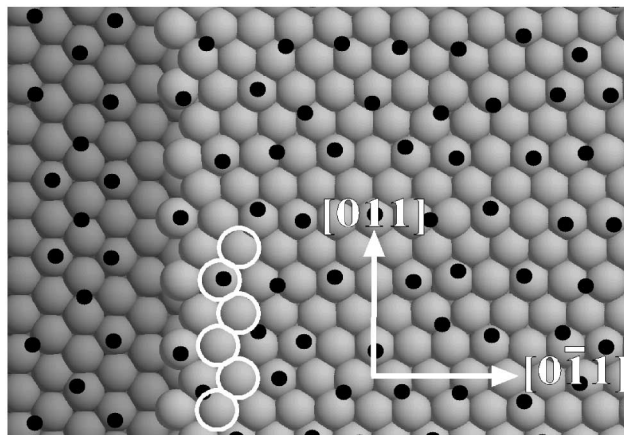


FIG. 1. Top view of Pt(100)-hex with CO adsorbed (represented by the smaller black dots). Darker colors correspond to lower levels. The (5 × 1) unit cell, indicated by the white circles where six atoms are on top of five substrate atoms in the [011] direction, is used in our simulations to model the real (5 × 29) quasihexagonal periodic unit cells (Ref. [3]).

CO on Pt [11]. Theoretical modeling using lattice-gas methods, such as Monte Carlo simulations, has been successfully applied to study the oscillatory behavior of CO on Pt(100) [12–16] as well as the CO-induced lifting of the Pt(110)-(2 × 1) missing row reconstruction [17]. Lattice-gas simulations, however, are possible only when the system undergoes rearrangement of atoms on a fixed, predefined lattice. It is precisely the absence of such a fixed lattice in the hex → (1 × 1) phase transition which makes it impossible to study the restructuring process on Pt(100) with lattice-gas methods.

Recently, we have shown that molecular simulations using the modified embedded-atom method (MEAM) [18], are able to describe a wide range of surface properties of transition metals [19,20]. It is this method that, in terms of number of particles and time scale, allows in principle investigation of systems at the required scale, such as the adsorbate-induced lifting of a surface reconstruction. We have developed a potential parametrization for the CO/Pt system, based on DFT calculations as well as experimental data, that correctly takes into account the CO-CO lateral interaction and adsorption energies of CO at different surface sites on the (100) and (111) surfaces [20]. The adsorption energy of CO on the (100)-hex surface phase was, however, not included in the parameter fit data. The difference in adsorption energy on the (1 × 1) and hex phases of Pt(100)—with our current MEAM parametrization 0.2 eV/atom—is believed to be the driving force of the surface restructuring and is therefore crucial in correct modeling of this system. It is worth noting that here we treat the CO molecule as an effective atom. This can be justified when one realizes that CO binds only to the Pt surface through the C atom. Further, in vacuum, the hex phase is predicted by our MEAM potential to be favored over the (1 × 1) phase by 0.1 eV/atom, which agrees reasonably well with the experimental value of 0.2 eV/atom [21].

In our MD simulations, with time steps of 1 fs, we applied higher values for the temperature and the local CO coverage than was used experimentally, in order to accelerate the restructuring process: the CO coverage  $\theta$  was varied between 0.4 and 0.5 ML. After equilibrating at 100 K, the simulation temperatures were raised to values between 750 and 950 K. In all cases, similar behavior was observed. The simulations were performed using periodic seven-layered slabs with two perpendicular oriented hex domains, of which one is elevated one layer to mimic a step, see Fig. 1, making a total of 1800 surface atoms. No constraints have been imposed on the atoms in each slab, except for the bottom layer, which has been kept fixed. The hex reconstruction is modeled by (5 × 1) unit cells on top of a (1 × 1) substrate. These (5 × 1) unit cells are for our purposes equivalent to the larger (5 × 29) unit cells—i.e., with respect to the restructuring mechanism and surface energies—but allow for smaller simulation slabs, and hence longer simulation times (up to 1 ns) and better statistics.

Our simulations reveal a restructuring mechanism that is collective in nature, in the sense that entire chains of Pt atoms are squeezed out of the hex surface and forced up to become adatoms, allowing the remaining surface atoms to rearrange and adopt the bulk-terminated square symmetry. These chains constitute the ~20% excess atoms; see Fig. 2.

A closer inspection reveals that the rows of surface atoms that are ejected are typically the ones which are, due to the misfit between atoms in the hex and square planes, closest to an on-top position with respect to the second layer atoms. Each two rows adjacent to these on-top surface rows close in through a zipperlike action to become neighboring rows and thereby sequentially forcing up the on-top atoms. From Fig. 2, the ejection occurs on the order of a few atoms per ps. In contrast, inspection of the trajectory of every CO molecule indicates that CO jumps 4 to 6 times on average, during the entire simulation time of 0.5 ns. In agreement with STM observations

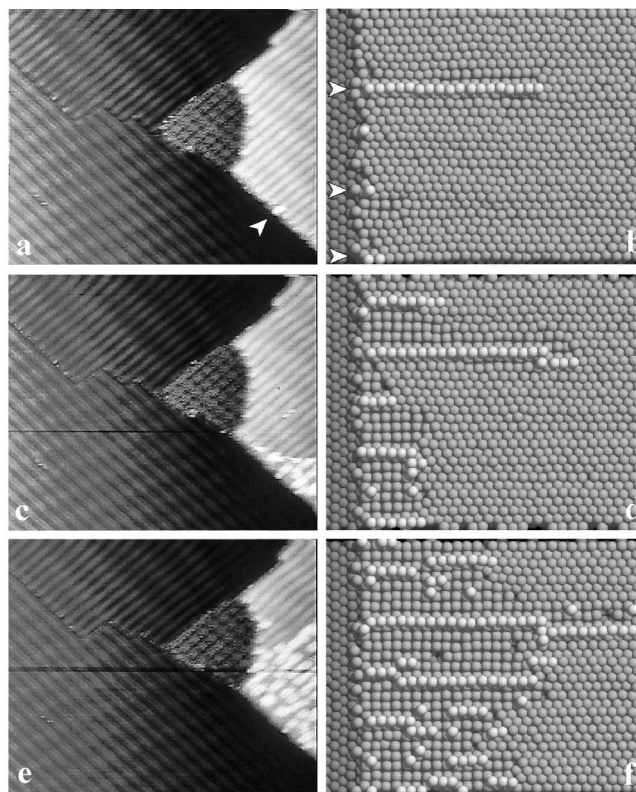


FIG. 2. Successive STM and MD/MEAM simulation snapshots of the initial CO-induced lifting of the Pt(100)-hex reconstruction. The CO exposure in the STM images (a), (c), and (e) ranges from 0.2 to 1.2 L, 1 L =  $10^{-6}$  Torr · s (for further experimental details, see Ref. [9]). In the simulation images (b), (d), and (f), the CO coverage is 0.5 ML. For clarity CO is not shown. The simulation snapshots cover a simulation time of ~0.5 ns. The simulation results clearly indicate that the observed anisotropy in the STM measurements is caused by chains of surface atoms being collectively ejected, nucleated at the step (marked by the arrows).

[9], the phase transition is found to be heterogeneously nucleated. The nucleation centers are linear defects such as steps, causing disruption of the hexagonal structure in the  $[0\bar{1}1]$ -trough direction (i.e., the step edge is aligned along the  $[011]$  direction). We should note, however, that homogeneous nucleation was also found to be possible in our simulations on a planar, nonstepped surface, but requires a higher activation energy and proceeds at a much lower rate (for an accurate investigation even beyond our current computational possibilities).

The phenomenon of ejected chains and their nucleation only at “perpendicular”  $[011]$  steps is easily explained when one considers the activation of such a process: ejecting a single Pt atom would involve more Pt-Pt bonds to be broken and is therefore energetically less favorable. Furthermore, perpendicular steps enhance the ejection, since one end of the chain to be ejected is already disconnected from the hex surface. In addition to that, the step energy of these more open, perpendicular steps is higher than the step energy of the more closed steps parallel to  $[0\bar{1}1]$  (approximately  $0.1 \text{ eV}/\text{\AA}$  according to our MEAM potential), which means that the steps parallel to  $[011]$  are less favorable and thus more prone to rearrangement. This also explains why Ritter and co-workers [22] in their STM measurements on a part of the surface with only “inert” steps along  $[0\bar{1}1]$  did not see nucleation at these steps.

The activation energy  $E_a$  of the restructuring process can be determined using Arrhenius’s law. The  $(1 \times 1)$  growth rate  $r$  is related to temperature  $T$  by

$$r = r_0 \exp(-E_a/k_B T). \quad (1)$$

$E_a$  is found to be  $0.45 \pm 0.1 \text{ eV}$  at  $\theta = 0.5 \text{ ML}$  (Fig. 3). This rather modest value for  $E_a$  agrees with the experimental observation of restructuring occurring at temperatures as low as  $150 \text{ K}$  [23]. This is to be compared with the  $(1 \times 1) \rightarrow \text{hex}$  transition on clean Pt(100), which has an activation energy of about  $1 \text{ eV}$  and occurs only around  $400 \text{ K}$  [24]. When varying the CO coverage  $\theta$  on the initial hex surface, the growth rate  $r$  is found to vary nonlinearly with  $\theta$ , but due to the large statistical error in our results, the order  $\nu$  of the reaction cannot be specified better than  $\nu = 7.5 \pm 2.5$ , Fig. 4. The nonlinear dependence is in line with experiment, where the relation  $r \propto \theta^\nu$ ,  $\nu = 4.5 \pm 0.4$  was found [10]. It is interesting to realize that at the higher coverages employed in our simulations, we do not find evidence for a simple kinetic model as suggested by Hopkinson *et al.* [10] and Ali *et al.* [25], where four to five CO molecules approach and somehow locally convert a few Pt atoms with hexagonal symmetry, to become square. In our simulations, no local clustering of four to five (or, from our value of  $\nu$ , five to ten) CO molecules is observed at the nucleation centers of the phase transformation (Fig. 5). This suggests highly complex kinetics are involved and, in contrast to the empirical model described above, the mechanism observed here is not diffusion limited in the sense that a

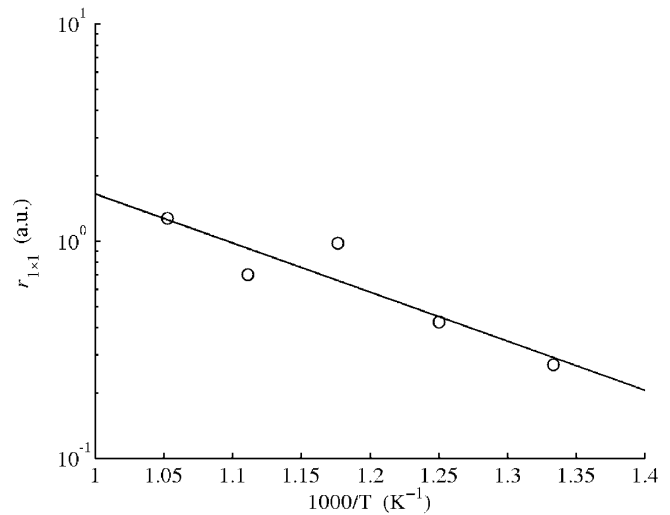


FIG. 3. Arrhenius plot of the rate of the restructuring process at  $\theta = 0.5 \text{ ML}$ . The activation energy  $E_a$  is found to be  $0.45 \pm 0.1 \text{ eV}$ .

certain number of CO molecules should cluster in order to initiate restructuring. It appears from our simulation results that the adsorbed CO molecules initiate surface relaxations and a shear tension between adjacent  $[0\bar{1}1]$  rows, due to the preference for a square over a hexagonal coordination sphere. This creates an environment in which Pt atoms can be sequentially squeezed out of the surface to form chains of adatoms, and realignment of the remaining surface area becomes possible. With this cooperative ejection and rearrangement of Pt atoms, the entire concentration of CO molecules in the vicinity to the critical area is involved, since, in general, surface relaxations and tension are not restricted to a few atoms only, but extend over several atomic distances.

The results addressed above are in line with the Monte Carlo simulations by Kuzovkov *et al.* [26], who managed

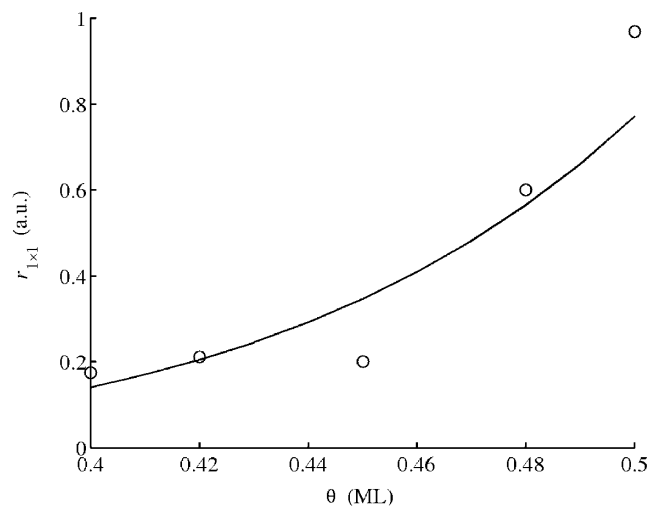


FIG. 4. Restructuring rate  $r$  as a function of CO coverage. The drawn line represents the nonlinear relationship:  $r \propto \theta^{7.5 \pm 2.5}$ .

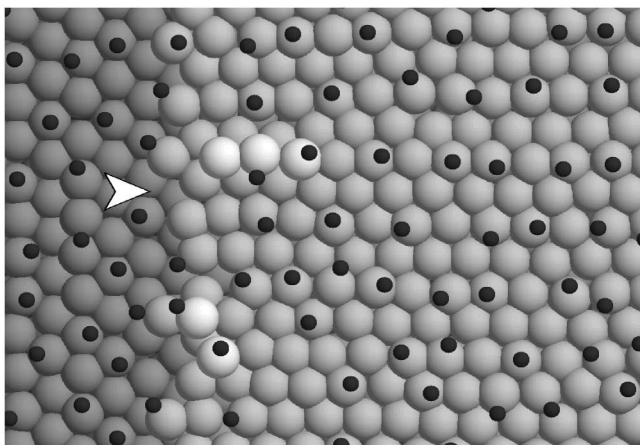


FIG. 5. Snapshot of the initial stage of the restructuring of Pt(100)-hex ( $\theta = 0.4$  ML). The smaller black dots represent CO. As seen there is no significant clustering of CO molecules around the nucleation center at the step, marked by the arrow.

to reproduce the nonlinear coverage dependence of the growth rate as well, using a model in which the phase transition is nucleated by cooperative processes, without any local clustering of CO.

In conclusion, the first atomistic simulations of the CO-induced lifting of the Pt(100)-hex reconstruction have been performed and the results indicate that the restructuring proceeds through cooperative ejection of chains of Pt atoms and rearrangement of the remaining surface atoms. These chains, representing the  $\sim 20\%$  difference in atomic density between the two phases, explain the anisotropy of the restructuring process. This mechanism resembles the mechanism proposed by Mase *et al.* [27] for NO on Pt(100)-hex. The phase transformation is heterogeneously nucleated at linear defects, as concluded by Borg *et al.* [9], with an effective activation energy of  $0.45 \pm 0.1$  eV, although homogeneous nucleation is possible at higher activation energies. The coverage dependence of the growth rate of these heterogeneously nucleated ( $1 \times 1$ ) domains is nonlinear but cannot be explained—at least at higher coverages—in terms of elementary reaction kinetics as proposed by Hopkinson *et al.* [10] and Ali *et al.* [25]. This nonlinear behavior is rather explained in terms of CO-induced relaxations and a shear tension between the  $[0\bar{1}1]$  rows of Pt atoms in the surface layer and the subsequent collective restructuring process.

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