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CO-induced structural changes of Pd particle surfaces

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The interaction of CO with Pd particle surfaces has been studied by means by field ion microscopy (FIM). CO-induced structural changes ranging from well defined reconstructions of individual surface planes to a reshaping of the apex crystal have been made visible with atomic resolution. For example, after reaction with CO at 1 hPa and at 300 K, the {011} and {113} surface planes, still covered by CO_{ad}, are found to exhibit the (1×2) missing row structure in which every second chain of atoms is removed. Other high index planes in the transition region between the low index {111} and {001} planes have dissolved in the presence of adsorbed CO and form facets, the terraces of which again contain the densely packed planes. The adsorbate-induced changes are explained on the basis of earlier mass spectrometric and kinetic investigations by means of atom-probe techniques according to which adsorbed subcarbonyl entities, $Pd(CO)_{2,3}$, liberated from kink site positions, diffuse across the surface until they decompose at favourable sites.

Keywords: Adsorbate-induced reconstructions; real-space imaging; field ion microscopy

1. Introduction

It is well known that adsorbates can cause structural modifications of transition metal surfaces ranging from small perturbations in the interatomic distances to topographic changes with respect to the underlying bulk structure [1,2]. The detailed knowledge of these changes seems to be a prerequisite for the development of realistic models of chemical surface reactions as these are expected to be sensitive to both the nature of the reactants and the atomic structure of the substrate.

A great deal of the present-day knowledge of reconstructions on single crystal surfaces is based on results obtained by low electron energy diffraction (LEED). While a complete *I/V* analysis of LEED data may be cumbersome in many cases, the application of real-space methods capable of providing atomic scale information seems to be rather straightforward. For example, scanning tunneling microscopy (STM) has been recently applied to study the CO-induced transformation of the (1 × 2) reconstructed Pt{110} plane into the (1 × 1) bulkterminated form [3]. Field ion microscopy (FIM) [4,5], as another example, has been shown to be capable of imaging reconstructions of surface planes containing only a few atoms. The hydrogen-induced formation of a (1 × 2) missing row structure with only 9 atoms on top of a Ni{110} field emitter plane has been made visible by means of this method [6].

Both examples demonstrate that the presence of adsorbates can cause or lift surface reconstructions. The microscopic mechanism of these changes seems still to be a matter of debate, although experimental data in case of the CO-induced (1 × 2) to (1 × 1) transition on Pt{110} at 300 K clearly favour a homogeneous nucleation process involving atomic motion over only a few lattice sites [3].

Recently, evidence has been obtained from LEED and infrared data [7] that the adsorption of CO on Pd{110} can cause a (1 × 1) to (1 × 2) reconstruction which is reversible and dependent on the surface coverage. No reproducible LEED patterns, however, could be obtained for CO on Pd{113} [8]. The present investigation by means of FIM is aimed at providing experimental proof that both surface planes, Pd{110} and {113}, form missing row arrangements in the presence of adsorbed CO.

Furthermore, it will be shown that, for these conditions, also the high index vicinal Pd planes are unstable and undergo structural changes. As a field emitter tip can be considered a realistic model of a relatively large catalyst particle, FIM of adsorbate-induced reconstructions of individual planes embedded in overall morphological changes may provide the link to studies with uniformly oriented single crystal surfaces.

2. Experimental

The experimental set-up used for this investigation was a two chamber stainless steel system consisting of an ultrahigh-vacuum (UHV) field ion microscope (FIM) and a reaction chamber. The residual gas pressure in the FIM chamber was always below 5×10^{-9} Pa and largely dominated by hydrogen as revealed by quadrupole mass spectrometry. A channel-plate ($\phi = 3$ inch) for image intensification was mounted on a movable rod in order to adjust the distance to the field emitter tips. Samples were cooled by liquid N_2 or He in thermal contact with the sample assembly. The Pd samples were mounted on a four-lead holder, which allowed for heating and temperature measurements (by means of a thermocouple spotwelded to the shank of the field emitter tips). Field ion micrographs were continuously monitored by means of a highly sensitive video recording system. Individual micrographs could be digitized and transferred to a host computer for storage. The software package allowed for a detailed analysis of the micrographs, including the determination of relative atomic distances before and after reaction of CO with the Pd samples.

Samples could be transferred under UHV between the two chambers by means of a magnetically coupled rod. The reaction chamber was equipped with a differentially pumped mass spectrometer which allowed one to monitor the evolution of gaseous species originating from the sample surface. The base pressure in the reaction chamber was routinely in the lower 10^{-7} Pa range. CO gas (impurity concentration below 0.1 ppm) was introduced into the reaction chamber after freezing out impurities in a molecular sieve cooled by liquid N_2.

Pd tips were prepared from a polycrystalline Pd wire (J. Matthey, 'puratronic quality) by electropolishing in conc. HCl/conc. HNO_3 (30 : 70 v/v). In order to prevent the embrittlement of the Pd by absorption of hydrogen [9] formed during the etching process, the samples were prepared by strictly anodic etching of the wires. Furthermore, the concentration of hydrogen dissolved in the etching solution was kept as low as possible. In order to obtain clean surfaces, Pd tips were treated in UHV by combined field evaporation and Ne-sputtering at 85 K. Crystal defects could be eliminated successfully by heating the emitter specimens in UHV to 600 K during several hours. Only samples free of grain boundaries or similar structural defects in the apex region were submitted to reaction experiments with CO. Before introduction into the FIM chamber the Ne imaging gas was further purified in a molecular sieve cooled by liquid N_2.

3. Results

Fig. 1 shows a Ne field ion micrograph along with a stereographic projection of an {011} oriented Pd tip (in quarter space) with a radius of curvature of approximately 20 nm. No structural defects are visible. The tip surface is apparently clean and contains the various crystallographic planes, i.e. {111}, {011}, {001}, {012} and {113} with the respective (1×1) arrangements of the inner atoms. Such a tip surface, developed by field evaporation, was always the starting point for the reaction studies with CO. The FIM image in fig. 1 is slightly blurred because it was taken at 31 V/nm which is below the best image field strength of Ne (37 V/nm). In order to differentiate between thermal effects and CO-induced structural changes of the surface, blank experiments were performed by heating the Pd crystal to temperatures of up to 350 K. Subsequent imaging of the sample in Ne at 85 K resulted in micrographs almost identical to the one shown in fig. 1.

The Pd field emitter tip, prepared as described above, was transferred into the reaction chamber and subjected to reaction with CO at 300 K and $p = 1$ hPa during 6 h. The composition of the gas phase during the reaction was mass spectrometrically monitored. No species other than CO and its fragments appeared in the mass spectrum. After the back-transfer into the FIM chamber, the tip specimen was imaged in Ne at 85 K which resulted in the micrograph shown in fig. 2. At the field strength used (26 V/nm), the image pattern turned

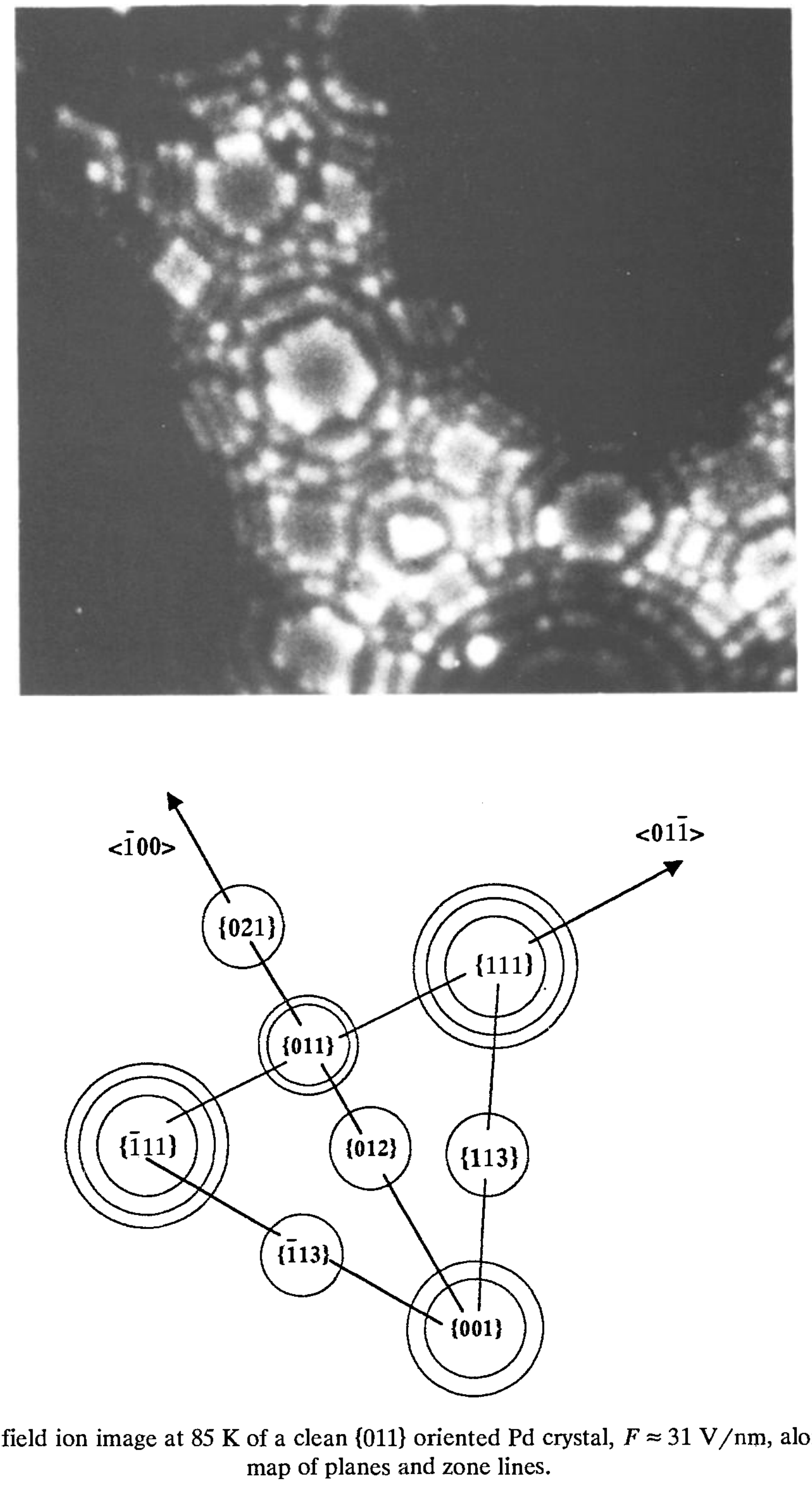

Fig. 1. Ne-field ion image at 85 K of a clean {011} oriented Pd crystal, $F \approx 31$ V/nm, along with a map of planes and zone lines.

out to be stable during several hours of experiment in the high electric field. Compared to the tip structure before the reaction, conspicuous structural alterations are observed after the reaction. In particular, the high index planes in the transition region between the low index {111} and {001} planes have undergone restructuring in a manner most easily described as faceting. For example, the inner of the formerly present {133} planes, located along the $\langle 01\bar{1}\rangle$ zone line between {110} and {111}, remains dark in fig. 2. This is expected for facets with densely packed terrace atoms. Quite complicated surface structures are observed in the {021} region where chains of atoms with different orientation come together and form junctions. Again, the distances between the image patterns are widened and the terraces of the facets remain invisible. As a general result of the restructuring, the total number of step atoms in the high index planes is drastically reduced.

A particularly well defined CO-induced reconstruction is observed to occur in the region of {011}. This is demonstrated by comparing figs. 1 and 2. In fig. 1 only atoms at the edge but not of the inner part of the {011} plane are visible. Atomic resolution could be achieved when reducing the size of the plane by controlled field evaporation. For the measurements reported here, larger planes were preferred in order to avoid possible size effects in the structural changes of these surface planes. After reaction with CO the (1×1) arrangement of atoms in the {011} plane appears to be transformed into a (1×2) missing row arrangement in which the atomic chains lie in alternate channels of the underlying plane. Note that the size of the {011} plane remains nearly unchanged by the reaction with CO. There are also indications that the chemical etching process removes, from the outside to the inner (but confined to the ledge plane), atoms of the underlying first or second {011} layer. The bright spots appearing in fig. 2 are unlikely to be caused by carbon/oxygen formed during chemical decomposition of adsorbed CO, as this process has recently been shown to occur at considerably higher temperatures than used here [10].

Imaging of surface reconstructions in FIM was performed in the presence of adsorbed CO. It was shown elsewhere [11] that removal of the adsorbate requires field strengths close to the onset of field evaporation of the substrate material. Despite being the subject of intense discussions in the earlier days of field ionisation and its applications in surface science [12,13], it is now well accepted that CO_{ad} remains invisible in FIM.

The (1×2) reconstruction of the {011} plane turned out to be stable up to field strengths of 28 V/nm. No adsorption or desorption of species could be detected even for extended periods of imaging. After field evaporation of only the topmost layer, i.e. of the Pd ridge atoms of the reconstructed surface, the (1×1) atomic arrangement of fig. 1 appeared again. Interestingly, also the {113} plane seems to undergo topographical changes during the reaction with CO. The respective pattern structures in fig. 2 are quite dim, however, with increasing field strength their quality improved considerably so that a (1×2) missing

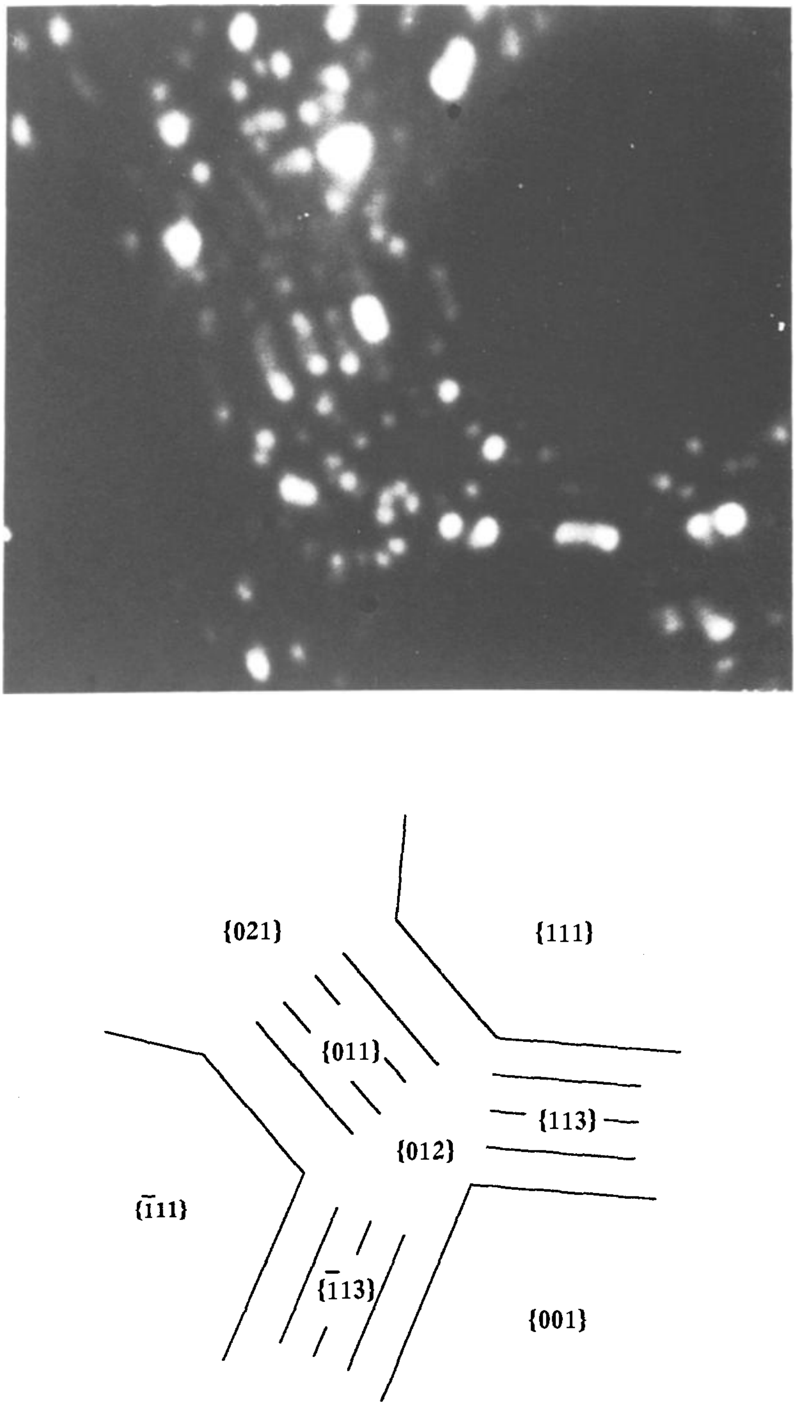

Fig. 2. Ne-field ion image at 85 K of a clean {011} oriented Pd crystal, $F \approx 26$ V/nm, along with a scheme of structural changes.

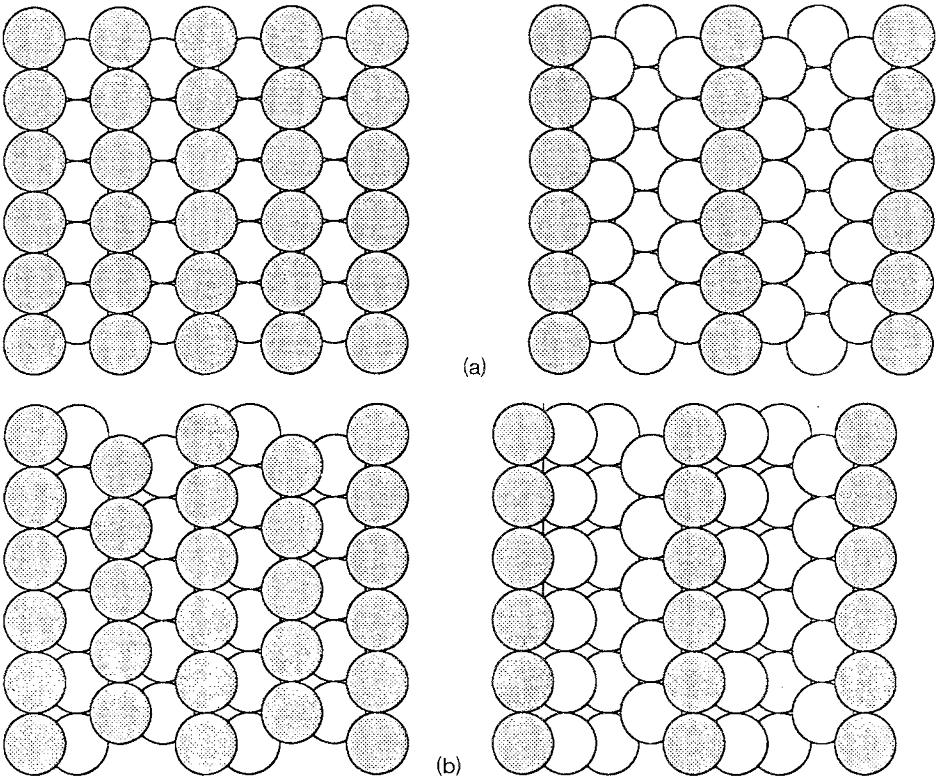

Fig. 3. Ball models of the (1×1) and (1×2) structures on fcc {011} (a) and fcc {113} (b).

row type reconstruction could be clearly identified [14]. A schematic illustration of the {1 × 2} reconstructions of Pd{011} and {113} is given in fig. 3. Obviously, the microfacets of the {011} plane are made up of {111} oriented slopes. The reconstructed {113} plane, however, contains alternating {001} and {111} oriented slopes.

4. Discussion

The results described above have demonstrated that the nearly hemispherical apex of a Pd field emitter tip is subject to considerable reshaping in the presence of adsorbed CO. The high index planes form facet structures, edges of which can be imaged in FIM. Ball models show that the terrace parts of the facets consist of atomically smooth, i.e. energetically favourable low index {111} and {100} planes.

When increasing the field strength to values higher than those reported here [14], the ring systems of the CO-covered low index poles have been gradually revealed. In this manner it has been checked that the number of these rings is the same as before the reaction with CO and that changes are confined to the high index transition regions. Generally, if the ring systems become wider there, the step heights must increase from mono- to multiple-atomic (also called the coarsening of the crystal) depending on the particular facet structure. Obviously, the total surface area seems to increase during these morphological changes, however, the total surface free energy is reduced because the faceting leads to the formation of terrace planes with low specific surface free energy.

The conclusion that the structural changes of the apex surface are induced by adsorbed CO can be drawn because thermal etching effects at 300 K have turned out to be negligible. Furthermore, the considerable mass transport of Pd can only be achieved through surface diffusion. In a FIM study of the CO reaction with Ni field emitter tips [15] morphological changes, ultimately leading to truncated half-cubooctahedral forms of the apex, have been observed and associated with the dissolution of Ni due to the formation of $Ni(CO)_4$. Stable Pd-carbonyl compounds are not known to exist and, accordingly, have not been detected in the present study. However, adsorbed Pd-subcarbonyls, $Pd(CO)_{2,3}$, can be formed, provided the CO_{ad} coverages are sufficiently large. This has been demonstrated by pulsed field desorption mass spectrometry (PFDMS) [11] and will be discussed in more detail below.

Changes in the shape of particles along with formation of extended facet structures have been observed previously in numerous studies and are well documented in the literature (for a review, see [1]). However, only recently have structural changes been suspected to occur during the reaction of CO with alumina supported Pd particles [16]. The present FIM study, performed after reaction with CO at temperatures as low as 300 K and in the absence of a support material, has made these changes visible.

In certain regions of the particle surface, well defined facets have been made visible with atomic resolution. For example, the {011} and {113} planes assume (1 × 2) missing row reconstruction forms which are apparently stable even under conditions of saturated CO layers.

The finding that regular (1 × 2) missing row arrangements on {011} and {113} can be formed within the overall restructuring of the high index planes is remarkable. Generally, field ion micrographs show only the topmost atoms (preferentially those in edges), however, underlying layer atoms can be exposed by controlled field evaporation which occurs atom-by-atom starting from edge atoms and proceeding to the inner of the plane. In this manner we have observed that removal of the topmost ridge atoms of both reconstructed planes recovers the (1 × 1) initial structures.

The possibility of CO-induced structural changes of macroscopic Pd{110} single crystal surfaces has already been considered by He and Norton [18] and Raval et al. [7]. In particular, the latter authors assumed that a (1 × 2) missing row reconstruction forms in the medium range of CO_{ad} coverages but reverts back into the initial (1 × 1) structure at saturation. This reversibility has not been observed in the present study and, in fact, is not expected to occur because atoms removed to produce the missing row structure are irreversibly trapped in neighbouring planes of different crystallography.

It seems worth mentioning that extended FIM studies performed recently in this laboratory have shown that Rh single crystal particles also undergo strong reshaping in the presence of adsorbed CO [17]. The reaction temperatures applied in these studies are similar to those applied here, however, in contrast to the behaviour of Pd, missing row reconstructions of the {011} and {113} planes have, as yet, not been observed.

The microscopic mechanism envisaged to be responsible for the observed structural changes is based on the observation of mobile Pd-subcarbonyls in experiment with PFDMS [11]. The phenomenon of subcarbonyl formation, however, is not restricted to Pd but applies also to metals like Rh [19], Ru [20], Ni [21] and others. Time-resolved measurements by PFDMS have shown that the dicarbonyl species, $Me(CO)_2$, are always formed with a certain delay time depending on pressure and temperature. A reaction model has been proposed [20] in which the slow step of dicarbonyl formation is associated with the removal of a metal atom from the lattice site position (kink) and its diffusion into the terrace parts of the surface. Clearly, the decomposition of the subcarbonyl species in energetically favourable sites must lead to changes in the topography of the particle surface. The initial step in this reaction sequence, i.e. the transformation of a Me kink atom into an adsorbed Me-subcarbonyl represents a repeatable step which can be best described by the simple formula

$$\mathrm{MeCO_{kink} + CO_{ad} \rightarrow Me(CO)_{2,ad} + [\;]_{kink}}.$$

The process ends when an open chain of atoms is used up, i.e. when a kink site, $[\;]_{\mathrm{kink}}$, is not reproduced any more.

Based on the above reaction model, the formation of the missing row reconstruction on Pd{011} can be visualized as schematically sketched in fig. 4. Accordingly, the first kink atom, removed from the plane border, creates a local (1 × 2) patch with {111} oriented slopes. Presumably, the ridge atoms are energetically stabilized so that they are not able to undergo a similar process. The repetitive displacement of kink atoms in form of subcarbonyls followed by their migration along the troughs and by their trapping in neighbouring crystal planes leads to the observed (1 × 2) structure. One can imagine that the grooving process in parallel channels must not necessarily proceed as correlated as indicated in fig. 4. For example, the notching to produce local (1 × 2) patches can occur on opposite sides of the {011} plane edge, with the consequence that the repetitive removal of kink sites in opposite directions leads to reconstruction forms other than (1 × 2). This is the possible reason why in some cases irregular facet structures have been observed.

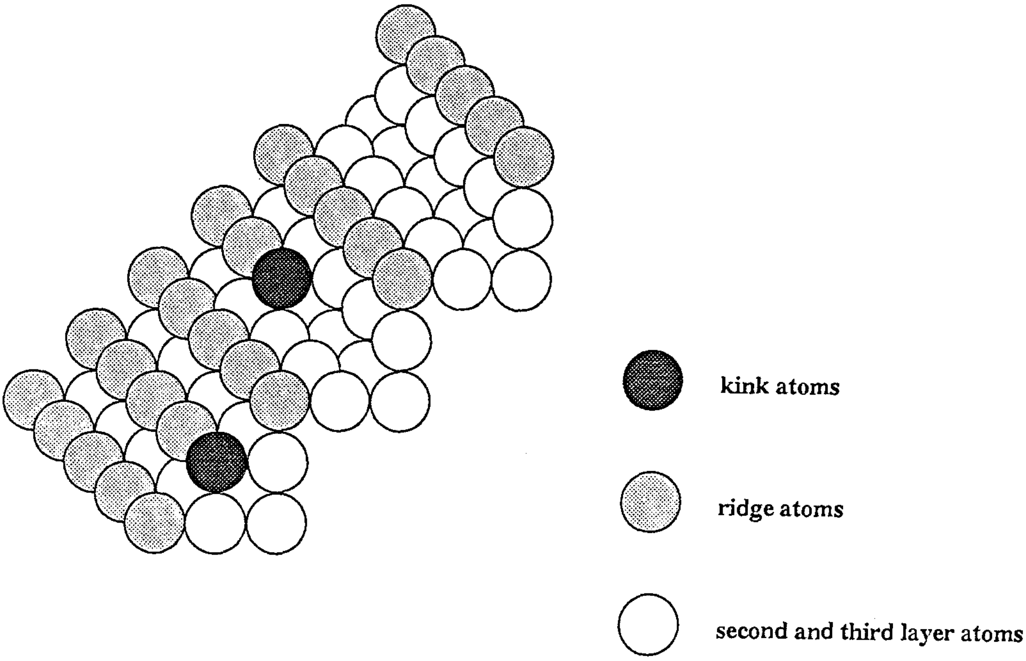

Fig. 4. Schematic drawing of the continuous removal of Pd kink site atoms as subcarbonyls.

In summary, we have imaged in real space for the first time the CO-induced structural changes of Pd particle surfaces. The resulting particle shapes can be described by a coarsening through facet formation in the high index regions. The facet terraces consist of atomically flat {111} and {001} planes. Assuming that these morphological changes always occur no matter what the detailed initial shape of the particle is, a structural model is provided which forms the basis to understand the phenomenon of structure insensitivity of certain catalytic reactions like the CO oxidation over noble metals.

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