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Dynamics of Adsorbate Islands with Nanoscale Resolution

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Surface catalytic processes produce, under certain conditions, small clusters of adsorbed atoms or groups, called *islands* which, after they have been formed, move as individual entities. Here we consider the catalytic reduction of NO with hydrogen on platinum. (i) Using video field ion microscopy, we observe the dynamic motion of small hydroxyl islands on the Pt(001) plane; despite changes in their morphology, the islands dimensions are confined to values corresponding to 10 to 30 Pt atoms suggesting cooperative effects to be in operation. (ii) We construct an automaton (or lattice Monte-Carlo) model on the basis of a set of elementary processes governing the microscopic dynamics. The agreement between the simulation results and the experimental observations suggests a possible mechanism for the formation and dynamics of hydroxyl islands.

KEY WORDS: Surface catalytic processes; adsorbate islands; field ion microscopy; cellular automata.

Modern surface science aims at elucidating the microscopic mechanisms of dynamic reaction phenomena.(1) Scanning tunneling microscopy (STM) has largely contributed to the development of the field by providing information at the atomic scale. For example, a recent study of the oxygen dissociation on the plane (111) of a platinum surface(2) has made visible the formation of adsorbate clusters called *islands*. Field ion microscopy (FIM) is an alternative method where samples are given in the form of small

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three-dimensional tips exposing a number of crystallographically different planes. The capability of the method to image dynamic reactive phenomena at nanoscale has been explored.[3–5] For example, reaction-diffusion fronts moving across the tip surface have been made visible thus providing information on the communication behavior of different planes. As compared to STM, the time resolution of the FIM method is only limited by the frequency of the video system (20 ms here).

While the formation and dynamical behavior of islands appear as a sequence of processes which, in general, are difficult to explain on the basis of a phenomenological description, this type of system is well suited for modeling with Cellular Automata,[6] which are constructed with simple rules, and may thereby suggest basic mechanisms for complex reactive phenomena. Here we report on FIM experiments showing the formation of small clusters of hydroxyl species from a co-adsorbed O_{ad}/H_{ad} layer on the (001) plane of a Pt tip surface during the reaction of nitric oxide (NO) with hydrogen gas, and, in order to gain insight into the basic mechanisms governing the fairly complex processes producing islands, we construct an automaton (or lattice Monte-Carlo model) with simple rules which offers a microscopic approach applicable to the experimental system studied by FIM.

The experimental studies were performed with a [001]-oriented Pt tip (metal purity 99.99%) prepared by electrochemical methods. The sample was mounted in an all-metal ultra-high vacuum (UHV) field ion microscope (base pressure 10^{-8} Pa) and cleaned using standard methods.[4, 7] Gases were used in either commercially available purity (NO: 99.5%) or after further purification using adsorption methods (H_2 and Ne: better than 99.999% each). Ne-field ion imaging prior to reaction experiments indicated a clean defect-free Pt tip. As described in ref. 4, the nearly hemispherical shape of the tip specimen is transformed into a pyramid during adsorption of NO gas or reaction with NO/H_2 gas mixtures, respectively. An essential feature of the pyramidal form is the appearance of large (111) oriented slopes and a (001) truncated top considerably increased in size as compared to the original state. Figure 1 shows a respective Ne-field ion image at 57 K obtained after the reaction studies. Only a few net planes are observed in the region between the (001) pole and the peripheral (111) planes. Subsequent to NO/H_2 reaction studies, a chemical surface analysis was performed using atom-probe techniques. The respective mass spectra[8] demonstrated the Pt tip surface to be oxidized, i.e., O_{ad}-covered. While in previous research, oscillating reaction phenomena with water (and nitrogen) product formation were examined in detail,[4, 5] we focus here on the occurrence of OH_{ad} islands from an O_{ad}/H_{ad} co-adsorbed layer, with particular emphasis on the dynamics of island formation and displacement on the Pt (001) pole.

The studies were performed under truly *in-situ* conditions, i.e., video field ion imaging during the ongoing surface reaction. Figure 2 shows a typical sequence of images as obtained while exposing an initially clean, nearly hemispherical Pt tip specimen to reactant pressures of $p_{H_2} = 4 \times 10^{-3}$ Pa and $p_{NO} = 3 \times 10^{-3}$ Pa at 500 K and 8.7 V/nm. After reaction-induced shape transformation into a pyramidal morphology small islands (appearing as dark patches on a bright background in Fig. 2) with an equivalent size of 10 to 30 Pt surface atoms become discernible on the (001) pole. Islands exclusively form at the layer edge and move into the (001) terrace region. Up to four islands can be seen at the same time. Mean lifetimes of several minutes are observed for individual islands before their annihilation at the layer ledge.

One of the interesting features in the genesis of small islands is their critical size. Accordingly, clusters extending over less than ~ 10 atoms of the Pt(001) plane are not observed. Conversely, spreading over more than ~ 30 Pt atoms does not occur either. Moving clusters yet suffer some changes in their morphology. Their simultaneous presence on the (001) plane may cause collisions; however, no mergence is seen. Under the experimental conditions applied, both NO and H_2 undergo dissociation on the Pt tip surface. The dissociation probability is strongly dependent on the local surface crystallography. Accordingly, starting with a clean surface, the Pt (001) plane is readily covered by O_{ad} (nitrogen atoms formed concomitantly

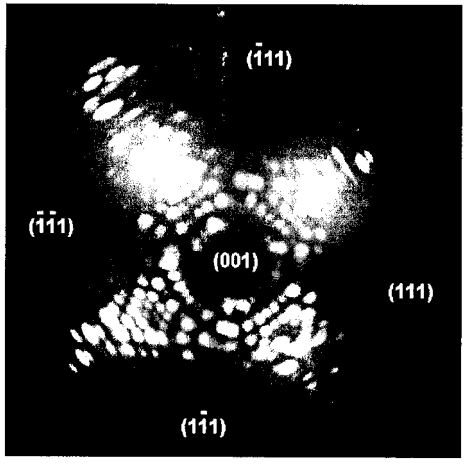

Fig. 1. Field ion micrograph (image gas: H_2) of a Pt tip demonstrating a truncated pyramidal form with a [001] oriented top; the morphology is the result of a NO-induced reconstruction of an originally hemispherical Pt specimen; the image was obtained after field evaporation of a few surface layers subsequent to reaction with NO/H_2 gas.

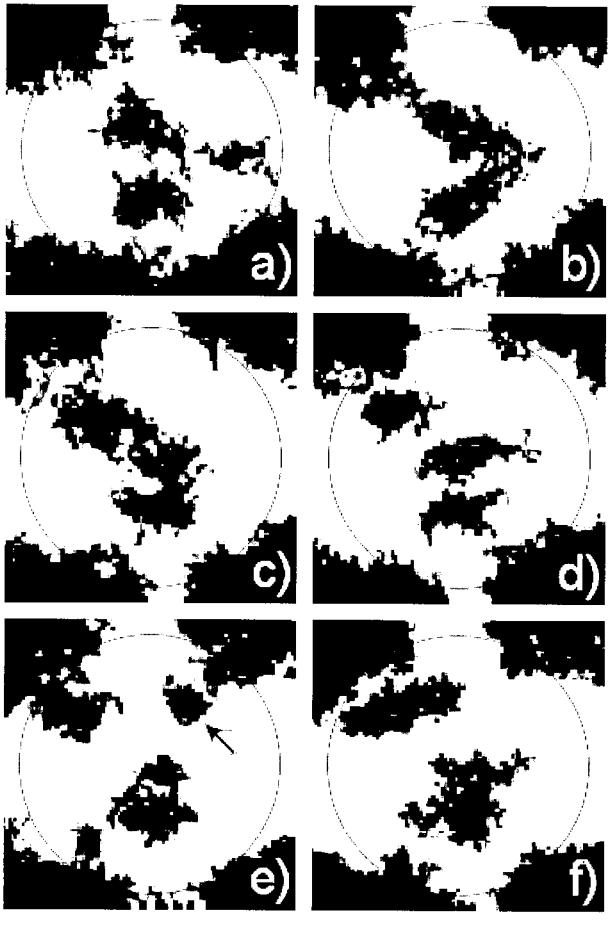

Fig. 2. Typical sequence of video field ion images demonstrating OH_{ad} island formation during the catalytic reduction of NO by H_2. Experimental conditions: $T = 500$ K, $p_{H_2} = 4 \times 10^{-3}$ Pa, $p_{NO} = 3 \times 10^{-3}$ Pa, $F = 8.5$ V/nm. Micrographs are treated by software allowing to optimize contrast and brightness; circles are understood as a guide to the eye to approximate the location of the (001) plane. Snapshots taken over a total time interval of order of 1 s demonstrate islands displacement, collision and separation; the arrow points to an island that will dissolve at the layer edge while proceeding to (f).

during NO decomposition undergo recombinative thermal desorption at the reaction temperature, $T = 500$ K[12–14]), while the rough surface planes accommodate both O_{ad} and H_{ad}. In fact, hydrogen activation at the (001) layer edge must be regarded as a critical step preceding H_{ad} injection into the O_{ad} covered (001) plane. Following the resonant field ionisation mechanism proposed by Kreuzer and Wang,[15] an oxygen-covered Pt

surface is expected to be imaged with considerable brightness when using molecular NO gas. On the other hand, hydroxyl species formed by reaction of O_{ad} with H_{ad}, are thought to be imaged with less brightness than O_{ad}, mainly because of the lower NO ionisation probability at slightly larger critical distances from the surface. The above arguments lead to the conclusion that OH_{ad} species are formed during the NO/H_2 reaction. They appear as small clusters with low FIM brightness in the "defect" region of the (001) layer edge and move collectively into the flat terrace region. One of the attractive features of the underlying reaction mechanism is the displacement of hydrogen islands on top of O_{ad} rather than exchanging O_{ad} for OH_{ad}. Alternative explanations according to which field-adsorbed water clusters are associated with the occurrence of FIM islands, can be rejected on the basis of results obtained for the O_2/H_2 reaction on Pt tips by field ion appearance potential spectroscopy.[5]

So far the microscopic mechanisms governing the dynamics of the experimentally observed phenomena described above have not been given a satisfactory explanation. A possible approach to the microscopic aspects of these surface reactive phenomena is provided by cellular automaton approaches[6] or lattice Monte-Carlo modeling.[17] Here we construct a cellular automaton[18] on a two-dimensional square lattice whose nodes can be occupied by virtual particles with exclusion principle (no more than one particle per node). The particles are subject to probabilistic motion with displacements along the four lattice directions: at each time step each particle can hop to any of its four nearest neighboring sites. The exclusion principle precludes simultaneous displacements of all the particles in the automaton universe in one time step. Therefore a sequential updating is implemented: the propagation phase consists of a sequence of successive displacements (on the average one per particle) and the *effective* time step is defined as the sum of N automaton time steps, where N is the number of particles in the automaton universe. Each particle can move to one of its neighboring sites, unless its destination site is occupied, in which case the particle does not move. The particles are subject to non-local two-body interactions, which are short-range attractive and long-range repulsive, and the amplitude and the range of the *attractive well* and of the *repulsive wall* can be tuned parametrically.

The justification of the automaton for the modeling of the surface phenomena observed in the experiments showing adsorbate islands, is as follows: (i) the processes take place in two-dimensional space, the Pt surface, and the (001) top plane has square symmetry (bulk-truncate form); the automaton reproduces these conditions as well as the size of the top plane (30 sites across); (ii) the restriction of a single hydroxyl group per site is accounted for by the exclusion principle; (iii) an hydroxyl group can

be identified as an automaton particle; (iv) the automaton has intrinsic fluctuations; (v) the particle dynamics depends on the interactions between OH groups (see caption of Fig. 3) which are short-range attractive and long-range repulsive.[19]

In the "vacuum" a particle has equal probability to move to any of its four neighboring sites; in the presence of other particles, this probability is biased according to the occupation of the sites within some *neighborhood* around the particle. The neighborhood is defined as the lattice domain surrounding an occupied site and containing all sites within interaction range. The bias is such that the sum of the probabilities at each site is conserved ($=1$) so that a positive (negative) interaction along one channel induces a repulsive (attractive) interaction along the other channels, and the propagation direction is drawn according to the probabilities evaluated, for the different channels, from the occupation of the lattice sites in the neighborhood.

The updating of the asynchronous automaton at each *effective* time step consists of a sequential series of operations. (i) An occupied site is chosen randomly; the probability that the particle be displaced to one of its four neighboring sites is initially set to 0.25 for each channel. (ii) The sites located within the neighborhood of the chosen particle are tested for the presence of particles, and the displacement probabilities are adjusted according to the position and distance of the particles within interaction range. (iii) In order to preserve the stochastic nature of the procedure, a random number is drawn between 0 and 1 and compared to the cumulated values of the probabilities of the successive channels; the channel for which the cumulated value exceeds the random number, is selected, (iv) The particle is displaced by one lattice unit along the selected channel, unless the destination site is occupied. (v) If so, the particle does not move, and the propagation probability is transfered to the target particle which memorizes one "collisional unit" in the corresponding channel for later updating; the initial probability for displacement (0.25) is then biased accordingly. This step in the algorithm acts as a process with momentum transfer memory.

The boundary, conditions of the automaton universe should be such that they correspond to the physical situation where hydrogen invades the Pt(001) surface from the adjacent planes, and particular properties must be assigned to the border nodes: a particle located on a site within a given distance of a border node is subject to a repulsive force which favors the particle displacement along the channels pointing inwards the system. This affects any particle residing on a site located at a distance equal or smaller than the border interaction range. Circular boundary conditions are imposed (i.e., a set of nodes with the boundary repulsive effect is chosen to

approach a circular geometry on the square lattice), and particles are injected in the form of bursts over a limited region of the boundary as follows. The circular boundary is ascribed a given arbitrary angular reference location where from an angle α is chosen randomly. The set of boundary sites in the arc spanned between α and a randomly chosen $\Delta\alpha$ define the region where particles are injected randomly during a time $\Delta\tau$; the time intervals between $\Delta\tau$'s are periodically distributed. The injection procedure is repeated for the duration of the simulation.

In Fig. 3 we present a sequence of snapshots from the model simulation starting with a burst injection and leading to the formation of islands and their subsequent evolution. Comparison with the experimental micrographs of Fig. 2 shows that the clusters obtained in the automaton simulation exhibit the essential features of the observed islands: their size (~ 30 sites) and number (3 to 4) have the correct order of magnitude, they remain "autonomous" (when in contact they do not merge), and their dynamics reflects the erratic motion of the islands. The agreement between the simulation results and the experimental observations suggests that the elementary processes on the basis of which the automaton is constructed, provide a plausible mechanism for island formation and dynamics as observed in FIM experiments whose results were awaiting satisfactory explanation. The basic mechanism responsible for the islands formation is

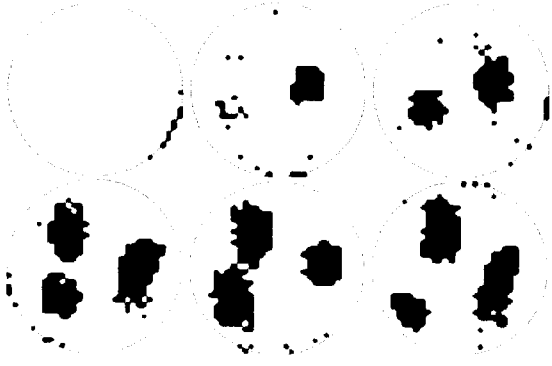

Fig. 3. Islands formation and dynamics in automaton with circular open boundary (diameter: 30 nodes). Interaction range and amplitudes: 9 nodes, with attraction on first 2 nodes and next 3 nodes, zero-interaction over next 2 nodes, and repulsion over last 2 nodes; relative values of the amplitudes: $-6:-3:0:+2$ respectively. Repulsion from boundary nodes: interaction range 9 nodes, with relative amplitude corresponding to 5% bias along the inward direction. Burst injection rate: 30 time steps every 100 time steps. The time sequence goes from left to right and from top row to bottom row: time $t = 1$ (upper left panel), 600, 1500, 3300, 5100, and 5700 (lower right panel) (t in automaton time step units). An animated version of the simulation is available on the web site http://poseidon.ulb.ac.be.

governed the balance between attractive and repulsive forces between OH_{ad} groups. The relative values of the interaction forces given in the caption of Fig. 3 give indication as to what a plausible interaction potential could be between OH_{ad} groups; furthermore we found the dynamics to be quite sensitive to the value of the parameters (for further explorations of surface aggregation phenomena by automaton simulations, see ref. 20), and the values used here optimize the agreement with the experimental observations. The other crucial feature is the role played by fluctuations as intrinsically contained in the automaton dynamics. So we conjecture that island formation and displacements are governed primarily (i) by the balance between lateral attractive and repulsive forces between OH_{ad} groups, and (ii) by dynamical fluctuations with memory effects caused by frustrated momentum transfer.

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REFERENCES

1. J. Wintterlin, S. Völkening, T. V. W. Janssens, T. Zambelli, and G. Ertl, *Science* **278**:1931 (1997).
2. Z. Zambelli, J. V. Bart, J. Wintterlin, and G. Ertl, *Nature* **390**:495 (1997).
3. V. Gorodetskii, W. Drachsel, and J. H. Block, *Catal. Lett.* **19**:223 (1993).
4. C. Voss and N. Kruse, *Appl. Surf. Sci.* **87/88**:127 (1994).
5. B. Sieben, G. Bozdech, N. Ernst, and J. H. Block, *Surf. Sci.* **167**:352 (1996).
6. J. P. Boon, D. Dab, R. Kapral, and A. Lawniczak, *Phys. Reps.* **173**:55 (1996).
7. A. Gaussmann and N. Kruse, *Catal. Lett.* **10**:305 (1991).
8. C. Voss, G. Abend, and N. Kruse, to be published.
9. K. Heinz, P. Heilmann, and K. Müller, *Z. Naturf.* **32a**:28 (1977).
10. M. A. Van Hove, R. J. Koestner, P. C. Stair, J. P. Biberian, L. L. Kesmodel, I. Bartos, and G. A. Somorjai, *Surf. Sci.* **103**:189 (1981); *ibid.* **103**:218 (1981).
11. H. P. Bonzel, G. Broden, and G. Pirug, *J. Catal.* **53**:96 (1978).
12. K. Schwaha and E. Berthold, *Surf. Sci.* **66**:383 (1977).
13. S. J. Lombardo, T. Fink, and R. Imbihl, *J. Chem. Phys.* **98**:5526 (1993).
14. D. Y. Zemlyanov, M. Y. Smirnov, V. V. Gorodetskii, and J. H. Block, *Surf. Sci.* **329**:61 (1995).
15. H. J. Kreuzer and R. L. C. Wang, *Z. Phys. Chem.* **202**:127 (1997).
16. L. K. Verheij, M. B. Hupschmidt, B. Poelsema, and G. Comsa, *Surf. Sci.* **233**:209 (1990).

17. V. P. Zhdanov, *Phys. Rev. E* **59**:6292 (1999), and references therein.
18. We use the general terminology *cellular automata* for the model described here by analogy with the *lattice gas automaton* approach used for the microscopic simulation of two-dimensional reaction-diffusion systems (ref. 6 above). The sequential updating in the present "automaton" makes the model equivalent to a lattice Monte-Carlo procedure.
19. A theoretical mesoscopic approach to model traveling nanostructures in surface reactions, based on the assumption of strong attractive adsorbate- adsorbate interactions, is presented in M. Hildebrand, A. S. Mikhailov, and G. Ertl, *Phys. Rev. Lett.* **81**:2602 (1998).
20. J. P. Boon, C. Bodenstein, and D. Hanon, *Int. J. Mod. Phys. C* **9**:1559 (1998).