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31 May 1996; accepted 18 July 1996

Identification of the "Active Sites" of a Surface-Catalyzed Reaction

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The dissociation of nitric oxide on a ruthenium(0001) surface was studied by scanning tunneling microscopy. The distribution of nitrogen atoms after the dissociation allowed the identification of the "active sites" for this reaction, which are formed by the low-coordinated, top metal atoms of atomic steps. It is proposed that their activity is caused by local changes in the electronic structure. The structure of the steps determines whether they remain active or become deactivated by oxygen atoms. The results demonstrate the complex manner in which the structure of a catalytic surface determines the reactivity of the catalyst and confirm the active sites concept.

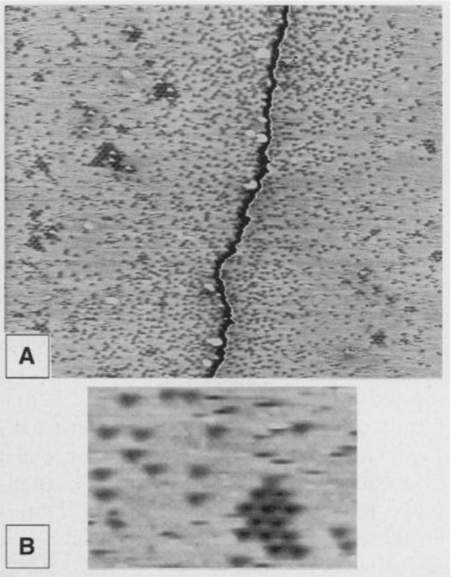

Fig. 1. STM images of a Ru(0001) surface after the dissociative adsorption of 0.3 L (1 L = 1 langmuir = 1.3×10^{-6} mbar·s) of NO at 315 K. The gray shading was done for the two terraces individually with brightness scaled according to height. Tunneling voltage (V_{sample}) = −0.6 V; tunneling current (I_{tunnel}) = 1 nA; T = 300 K. (**A**) Image (380 Å by 330 Å) showing two terraces (upper one to the left, lower one to the right) separated by a monatomic step (black stripe). (**B**) Close-up (60 Å by 40 Å) of the area marked in (A), showing an O island and individual N atoms. Individual O atoms are imaged as dashes (see arrow) parallel to the scan lines because most of them jump between subsequent scan lines.

The notion of "active sites" (*1*) is fundamental to heterogeneous catalysis. It reflects experimental evidence (*2, 3*) that many catalytic surfaces are not uniformly active but exhibit activity only at sites distinguished by a special arrangement of the surface atoms or by a special chemical composition. However, the exact nature of the active sites and hence the mechanism by which they act are still largely a matter of speculation. Taylor first formulated the idea in 1925 (*1*) that defect sites, formed by low-coordinated surface atoms with unsaturated valencies, are essential. The importance of defects is, in fact, indicated by the frequent variation of activity with particle size, which led to the classification of "structure-sensitive reactions" (*2, 3*). According to the Adlineationstheorie of Schwab and Pietsch (*4*), one-dimensional defects play a role. These might be identified with atomic steps, which were shown to accelerate chemical reactions on single-crystal surfaces (*5*). However, on the basis of considerations about electronic structure (*6*), it was suggested that the highly coordinated atoms at the bottom of the steps were the sites of enhanced activity, in contrast to the original idea. The validity of these concepts cannot be decided by the ordinary, laterally integrating methods, because the effects of defects as a whole are measured. It is therefore crucial to directly identify the atomic sites responsible for the active-site effect.

Here we present direct evidence by means of scanning tunneling microscopy (STM) for the active sites for the dissociative chemisorption of NO, a decisive step in the catalytic reduction of nitric oxides for which Ru is the most selective catalyst (*7*). A clean Ru(0001) sample was prepared under ultrahigh-vacuum conditions and exposed to NO at 300 K or slightly higher temperatures. It is known (*8, 9*) that under these conditions NO dissociates completely. The distribution of the chemisorbed N and O atoms thus formed on the surface was then investigated by STM at 300 K.

In the STM topograph of the Ru(0001) surface (Fig. 1A), taken 0.5 hour after exposure to 0.3 L of NO, a large number of small dark dots is discernible on both sides of a monoatomic step. The individual, disordered spots closer to the step represent N atoms, the small clusters at larger distances from the step are islands of O atoms, and the dark dashes are individual O atoms in equilibrium with the islands. This interpretation is based on experiments with pure N or O layers, in which it was found that O atoms partially cluster in islands with a (2 × 2) structure, whereas the N atoms are randomly distributed (*10*). In addition, the N and O atoms are imaged slightly differently by the STM, with the O atoms appearing black and the N atoms gray in the gray-scale representation of Fig. 1B (*11*). Individual N and O atoms can also be discriminated on the basis of their mobilities, the hopping rate of O atoms being comparable to the scanning frequency (this lets them appear as dashes in the images) whereas the N atoms hop only on the time scale of the full frames (*12*).

The distribution of the product atoms and their different mobilities suggest a mechanism according to which the NO molecules, which are extremely mobile and not detected by the STM at 300 K, have dissociated at the step into N and O atoms, whereafter the latter have rapidly diffused away from the step onto the terraces. The N atoms have moved away from the step more slowly, so that, when the image was recorded, a diffusion profile, with its origin at the step, could still be recognized. The N atoms thus serve as markers for the reaction sites (*13*). Therefore, the atomic steps, which exist with a finite density even on well-prepared, single-crystal surfaces, must be the active sites for the dissociation of NO

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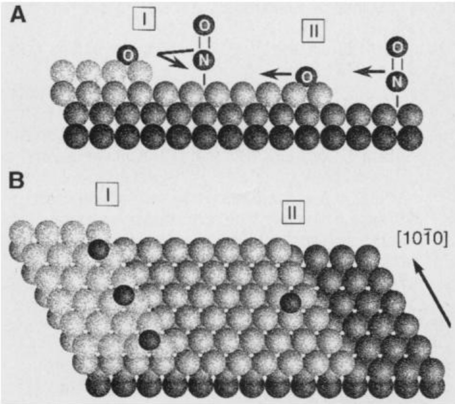

Fig. 2. (**A**) Side view of the surface, illustrating dissociation at a type II step and reflection of NO from an O-covered type I step. (**B**) Top view, indicating the structure differences between type I and type II steps: A metal atom at the type I step has one neighbor atom at the bottom of the step, whereas at the type II step it has two. For O atoms (small dark spheres) at type II steps there is a Ru atom between the atom and the step edge, whereas this is not so at type I steps.

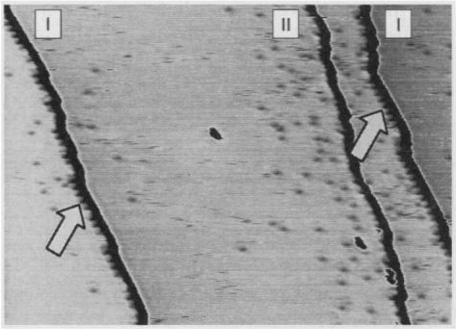

Fig. 3. STM image of a Ru(0001) surface after dissociative adsorption of 0.1 L of NO at 300 K; steps are descending from left to right (V_{sample} = −0.6 V; I_{tunnel} = 1 nA; area, 240 Å by 190 Å; 300 K). Gray spots are N atoms, rows of black spots with twofold lattice spacings directly at the steps are trapped O atoms (arrows), and dashes represent mobile O atoms on the terraces. For the narrow terrace between the type II and type I steps at the right side, it cannot be decided from which step the N atoms originate.

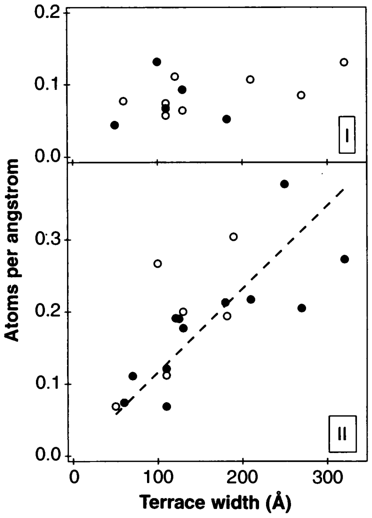

Fig. 4. Density of product N atoms near steps after exposure to 0.1 L of NO at 300 K versus the width of the adjoining terraces. Top: type I steps; bottom: type II steps. Open circles correspond to the adjoining top, filled circles to the bottom terraces. The broken line is a linear fit to the data points of the type II steps. Data are from 1450 N atoms from nine 400 Å by 400 Å STM images. Only terraces wide enough to allow clear attribution of the N atoms to the respective left or right step of a terrace were analyzed. The slow diffusion of the N atoms away from the steps limited the measurements to periods of the order of 1 hour after adsorption (depending on the terrace width).

on Ru(0001). Moreover, both sides of the step are covered with N atoms (Fig. 1A).

The Ru(0001) surface has two structurally different types of steps along [10$\bar{1}$0], which was the most frequent step direction on the sample (type I and II steps, see Fig. 2B). These steps differ also in their chemical behavior, as an STM topograph recorded after exposure to 0.1 L of NO illustrates (Fig. 3): Every other step has accumulated O atoms at its upper side, whereas O has moved away from the other steps. As before, the N atoms are still close to the steps at which they were formed. By STM images in which the Ru lattice was atomically resolved (not shown here), the steps decorated with O atoms were identified as type I steps. The difference can be understood from the fact that O atoms occupy only one of two possible threefold sites on the Ru(0001) surface, namely, that with another Ru atom underneath (*14*). These sites are oriented differently at the type I and II steps (Fig. 2B). In the case of the type I step, the step increases the strength of the O chemisorption and hence the residence time of the O atoms. If O atoms are present at the step, the reaction with further NO is blocked (Fig. 2A), as reflected by the larger number of N atoms on the central terrace near the type II step compared with the area around the type I step at the left side (Fig. 3). An additional aspect is the roughness of the steps; O chains form only at straight step segments along close-packed directions, and thus irregular steps may remain partially active.

We further analyzed the reactivity of the steps by correlating the density of N atoms in the regions near the steps with the width of the adjacent terraces (Fig. 4). From this analysis we drew three conclusions. (i) The scattering of the data is due to the fact that the steps are not perfectly straight and parallel so that the terrace width is not exactly defined. It is, nevertheless, obvious that there are significantly more N atoms at type II than at type I steps. (ii) In the case of the highly active type II steps the number of N atoms increases continuously with terrace width, whereas it levels off at a low value for the type I steps. (iii) There is no apparent difference between the upper and lower sides of both step types.

The data indicate that the type I steps are active for the dissociation of only a limited amount of NO. Larger terraces, corresponding to larger quantities of molecules, do not lead to additional product N atoms. Thus, the type I steps are self-poisoned by product O atoms that are trapped at the step edges. The contrasting behavior of the type II steps can be rationalized if a given fraction of the NO molecules that land at random positions on the surface diffuses across the terraces to these steps and dissociates before desorbing again (see illustration in Fig. 2A). If, in addition, the NO molecules remain largely on the terrace on which they first adsorbed before dissociation, the number of product N atoms at the steps must be proportional to the area, and hence the width, of the adjacent terraces, provided the steps are continuously active. This is actually the case for the type II steps. The fraction of molecules reacting in this way is quite large. From the slope of the linear fit to the data (Fig. 4), the fraction of molecules reacting is about 1/3; this value represents a lower limit because the STM tip partially shields the area under investigation from NO molecules from the gas phase. This value is in agreement with findings by surface-integrating methods of an initial sticking coefficient for NO of the order of unity (*15*) and with observations at low temperatures of a metastable, molecular adsorption state of NO, the existence of which is implied by the reaction sequence (*8*, *9*, *16*). The mechanism is also in agreement with the fact that surface diffusion and dissociation of adsorbed NO molecules can be estimated (*17*) to be several orders of magnitude faster than desorption, which is necessary to explain the large fraction of molecules that reach a step and dissociate. The operation of such a mechanism of trapping-mediated kinetics has also been postulated for other systems (*18*).

The fact that both terraces adjacent to a step are covered with comparable numbers of N atoms (Fig. 4) indicates that NO molecules approaching the step from both the lower and the upper adjoining terrace can react. This leads us to conclude that the reaction takes place primarily at the frontmost metal atom at the step. This is the only site that is accessible for the NO molecules from the upper and the lower terrace without crossing the step. This does not necessarily imply an identical transition state; the rough proportionality between the number of N atoms and terrace width rather suggests that the product atoms remain largely on the side from which the NO molecule approached the step. If the highly coordinated atoms at the bottom of the steps were active, as proposed in (*6*), the presence of the N atoms at the upper sides could not be accounted for. That the N atoms themselves move across the steps is ruled out by the finding that the numbers of N atoms on each side remained constant over at least 2 hours after NO adsorption. During this time only diffusion away from the step was observed (*12*). Interestingly, the result that the active sites are formed by low-coordinated atoms is in agreement with the original idea of Taylor (*1*).

We propose that the active-site effect during NO dissociation is caused by changes in the *d*-band local density of states (LDOS) at the Fermi energy E_F at the steps. Electronic structure calculations have shown that the chemical behavior of transition-metal surfaces is determined mostly by the *d* states (*19*, *20*); other theoretical studies suggested that the reactivity is connected with the E_F-LDOS (*21*–*23*). For the low-coordinated atoms at the top of steps the local *d* band narrows compared to the terraces (*21*). In Ru, which is close to the center of the transition-metal row of the periodic table where E_F intersects near the center of the *d* band, this leads to a larger density of *d* states at E_F (*24*). In the case of NO dissociation, the local reactivity is most likely governed by the extent of the backbonding between *d* orbitals and the antibonding NO π^* orbital, by analogy with CO (*25*). A larger *d*-LDOS should cause a more pronounced degree of backbonding, thus weakening the N–O bond and leading to an easier bond-breaking. This is similar to the effect of coadsorbed alkali atoms (*22*) for which a "softening" of the N–O bond has been observed (*26*). Electronegative coadsorbates such as O lead to a lowering of the E_F-LDOS and hence a reverse effect (*22*) that is reflected in a "stiffening" of the N–O bond (*9*). The deactivation of the type I steps by trapped O atoms is fully consistent with this picture.

These data directly confirm the concept of active sites in heterogeneous catalysis but demonstrate that the kinetics expressed as a "turnover frequency" (*2*, *3*) will be influenced by the microscopic surface structure and composition in a rather complex manner. For "real" catalysis under steady-state flow conditions, less active sites (for example, on terraces) will certainly come into play, so that the overall reactivity will be the result of weighted contributions from various surface structure elements, dominated by the active sites. This is, for example, reflected in the appreciably faster rate of hydrogenation of NO at 450 K on a stepped rather than on a flat Ru(0001) surface (*27*).

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21 May 1996; accepted 2 August 1996

Self-Assembly of a Two-Dimensional Superlattice of Molecularly Linked Metal Clusters

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Close-packed planar arrays of nanometer-diameter metal clusters that are covalently linked to each other by rigid, double-ended organic molecules have been self-assembled. Gold nanocrystals, each encapsulated by a monolayer of alkyl thiol molecules, were cast from a colloidal solution onto a flat substrate to form a close-packed cluster monolayer. Organic interconnects (aryl dithiols or aryl di-isonitriles) displaced the alkyl thiol molecules and covalently linked adjacent clusters in the monolayer to form a two-dimensional superlattice of metal quantum dots coupled by uniform tunnel junctions. Electrical conductance through such a superlattice of 3.7-nanometer-diameter gold clusters, deposited on a SiO_2 substrate in the gap between two gold contacts and linked by an aryl di-isonitrile [1,4-di(4-isocyanophenylethynyl)-2-ethylbenzene], exhibited nonlinear Coulomb charging behavior.

A structure of great interest for developing nanoscale electronics is a planar array of small metal islands separated from each other by tunnel barriers. Electronic conduction in such a structure can be varied from the metallic to the insulating limit by controlling the size of the islands and the strength of the coupling between them. Correlated single-electron tunneling (SET) in a patterned superlattice of this type has been proposed as a future basis for nanoelectronic digital circuits (*1*). However, if