

Scanning Tunneling Microscopy Investigations of Elementary Surface Processes

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Keywords: Scanning tunneling microscopy; elementary processes; adsorption; dissociation; reaction steps; diffusion.

Abstract.

A large fraction of processes which are at the foundation of our modern society involve physical and chemical properties of surfaces. This chapter describes a sample of some of the most relevant surface science studies which were recently carried out, in order to understand elementary surface processes at the atomic scale. The focus is on experiments performed by scanning tunneling microscopy (STM) that have represented, in some cases, real breakthroughs in our understanding of these phenomena.

Introduction

The last few atomic layers of a solid constitute its interface with the environment, and are essentially a two dimensional “playground” on which atoms and molecules continuously react by adsorbing, diffusing and desorbing. These processes form the very basis of several fundamental technologies on which our modern society relies for its prosperity. In environmental chemistry for example, catalytic processes are of vital importance for breaking down pollutants such as noxious automotive exhausts and industrial emissions. Similarly, most of modern industrial chemical production is based on catalytic reactions taking place on the surface of a suitable catalyst. Every year, more than 100 million tons of ammonia are produced by means of catalytic processes, and most of this chemical is converted into fertilizers for an increasingly hungry world. Atomic/molecular surface processes play also a key role in other economically important phenomena like semiconductor growth and technology, friction and lubrication, corrosion, and metal embrittlement.

The interest in improving our understanding of surface phenomena is therefore very strong. A more profound knowledge is the premise for optimizing, for example, the production rate and the selectivity of a catalyst and could be the key for mastering other promising technologies. In order to obtain an understanding of complex surface processes like catalytic reactions or the formation of metal-semiconductor interfaces, we need to know which are the various chemical species that participate in the process, how they are bound to the surface and what are the activation energies of the single elementary steps they go through.

The detection, identification and characterization of these elementary processes, however, is a tremendously challenging task. Ideally, in order to fully describe the diffusion and reaction of atoms and molecules on a surface, we need insight at atomic length scale and at the characteristic times of elementary step evolution (i.e. sub-picosecond time resolution), but we are still a long way from this goal. In order to address these challenging tasks, in the last 30 years or so, surface scientists have developed an arsenal of different experimental techniques [1].

Since its development about two decades ago, the scanning tunneling microscope (STM) has permitted to study the structure of conducting surfaces with unprecedented resolution [2]. In a further development, it was recently shown that under appropriate circumstances it can also be used to study insulating surfaces like diamond [3]. Most notably, atomic resolution was obtained on the 2×1 -C(100) surface by means of a resonant tunneling process [3]. Although it does not have a strong chemical sensitivity and in most cases it also lacks time resolution, the STM has proved to be a powerful tool in the study of adsorbate – surface interactions and of elementary surface processes in general [4].

In the following, we describe some very exciting results recently obtained by Scanning Tunneling Microscopy [2, 5], applied to the study of elementary surface processes.

Elementary phenomena at surfaces

The ensemble of surface phenomena which take place at a solid-gas interface is usually incredibly complex. Mainly for this reason surface scientists have basically confined themselves so far to the study of well characterized surfaces, which are obtained for example by cutting or cleaving a mono-crystalline sample along one of the planes with lowest Miller indices. In studying a single crystal surface, the idea is to examine samples with a well known geometry and a definite chemical identity. Obviously however, surface atoms do not always occupy ideal positions, and even the best prepared surface presents a large number of steps and kinks. At the outset we are therefore confronted with a basic problem: even model surfaces, prepared with the purpose of reducing the level of complexity, present a relatively large number of defects and/or other anomalies.

When a surface interacts with an external flux of atoms and/or molecules, many phenomena may take place; some of the most important ones are sketched in Fig. 1.

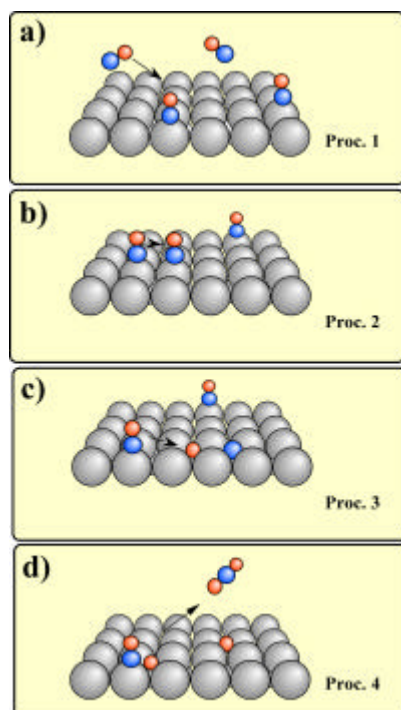


Fig. 1: Sketch of a number of elementary surface processes taking place on a surface exposed to an external atmosphere of reacting gases. (a) adsorption of a diatomic molecule (b) elementary step of diffusion (c) dissociation process (d) reaction step of combination between two adparticles, producing a molecule which is released in the gas phase. From Ref. [4], with permission.

Process N°1 shows a diatomic molecule which impinges on a surface. On hitting the surface it has a finite probability p of sticking to the surface and a probability $1 - p$ of bouncing back in the gas phase.

These molecules often form a chemical bond with the surface and choose a site which maximizes the binding energy. However, they do not reside long on the site where they have landed: if the surface temperature is high enough, they start migrating, jumping from one site to the next in a random way (see Process N°2 in Fig. 1), giving rise to a two-dimensional diffusion process.

The chemical bond formed by the molecule with the surface weakens considerably the intramolecular bond so that the molecule may end up dissociating into its constituents; these, in turn, stick to the surface with strong chemical bonds (Process N°3, Fig. 1). Atoms originating from the dissociation process are mobile on the surface and during their two-dimensional random walk, they may encounter other chemisorbed particles (atoms or molecules) with which they might combine forming new molecules, which may in turn leave the surface (Process N°4, Fig. 1).

A surface however is not simply an inert checkerboard. Upon adsorption of a foreign atom or molecule, it undergoes a local deformation; the atoms of the host surface, while forming new chemical bonds with guest particles, are forced to modify the structure of the bonds with the underlying bulk. For example, when Potassium is adsorbed on an Al(111) surface, it induces a rumpling of the first layer such that Al atoms directly beneath K atoms are displaced towards the bulk by as much as 0.25 Å [6]. For stronger interactions the adsorbate may cause a so-called *reconstruction* of the underlying surface, which can range from a simple distortion of the elementary cell, up to a complete rearrangement of surface atomic geometry.

An example of the first type of reconstruction is reported in Fig. 2b, where the distortion induced by Oxygen adsorption on Rh(100) is clearly visible. When coverage approaches half a monolayer, the elementary cell elongates from the original square to a rhombus and Oxygen sits in one of the corners forcing a new surface symmetry [7, 8]. For comparison, Fig. 2a shows a $c(2 \times 2)$ structure which is the most common formed by an adsorbate on a (100) surface of a face centered cubic crystal, at a coverage of 0.5 ML.

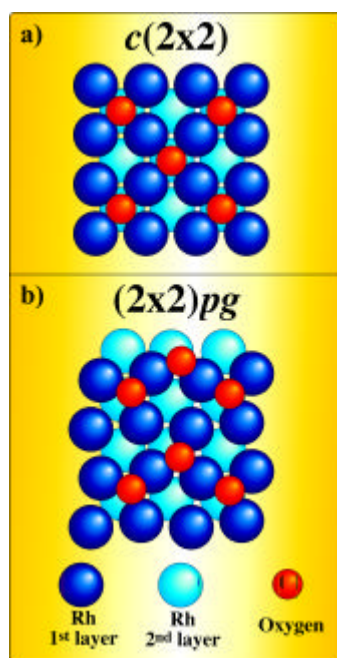


Fig. 2: Adsorbate over layers on a (100) f.c.c. metal surface at 0.5 ML coverage. (a) regular $c(2 \times 2)$ structure; (b) $(2 \times 2)_{pg}$ structure formed by oxygen on Rh(100). From Ref. [4], with permission.

In Figs 3a and b we report the structure of a Rh(110) surface and the same surface after 0.5 ML adsorption of Oxygen, respectively [9]. A considerable mass transport of Rhodium atoms takes place in this case and gives rise to a (2×1) “missing row” reconstruction¹, characterized by depressions three atomic

¹ (2×1) means that the periodicity in one direction is twice the original cell size, while the other remains the same.

steps deep. Surface reconstruction, whether spontaneously occurring or induced by an adsorbate, is an important phenomenon since it implies, besides a geometrical change, a strong long-range modification of electronic structure and chemical reactivity of the surface.

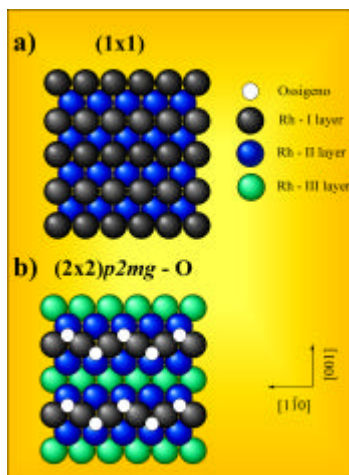


Fig. 3: Structure of a clean Rh(110) surface. (a) change of structure upon adsorption of 0.5 ML of Oxygen, (b) the reconstructed $(2 \times 2) p2mg - O$ implies a major process of mass transport during formation. From Ref. [4], with permission.

As mentioned above, structural information at the required spatial resolution (atomic or molecular scale) has been obtained by means of scanning probe techniques, which, as already noted, still have poor time resolution and a limited chemical sensitivity.

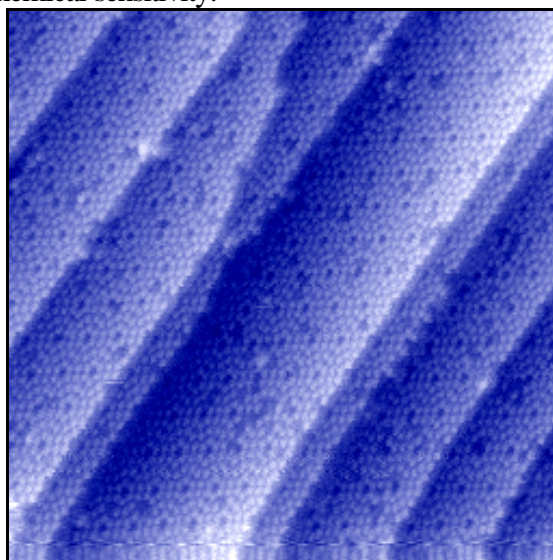


Fig. 4: STM image of a clean Si(111) surface (reconstructed 7×7). Sharp monoatomic steps are clearly visible. From Ref. [11] (F. Rosei, unpublished results).

The STM is generally capable of acquiring atom-resolved images of the uppermost surface layer of a conducting solid. Dramatic images of atomic arrangements have been obtained for a rather large number of metal and semiconductor surfaces. Most spectacular in the history of surface science has been the visualization of the geometric structure of the (7×7) reconstruction of the Si(111) surface [10], shown in Fig. 4 above [11]. In the following we present the information that was obtained on some of the elementary reaction steps depicted in Fig. 1.

Surface diffusion phenomena studied by STM

Recently, several impressive STM experiments were performed for characterizing diffusion processes of adparticles on surfaces (Process N°2 in Fig. 1b).

Previous macroscopic experiments for determining adsorbate diffusion constants have encountered severe difficulties. Even a well prepared single crystal surface in fact, exhibits defects (mostly atomic steps, kinks and impurities). Hopping energies at sites with different local structure may widely differ and a macroscopic experiment can only probe “effective” diffusion parameters averaged on many different elementary hopping processes.

By using newly developed fast STMs, capable of acquiring up to 20 images (typically $50 \times 50 \text{ \AA}^2$ wide) per second while still conserving atomic resolution, it was possible to follow the dynamic behaviour of individual guest atoms on several host metal surfaces [12-15]. The method implemented here consists in taking a long sequence of pictures of the same region of the surface and record those atoms which have moved (normally by one lattice parameter) between consecutive frames, as shown in Fig. 5.

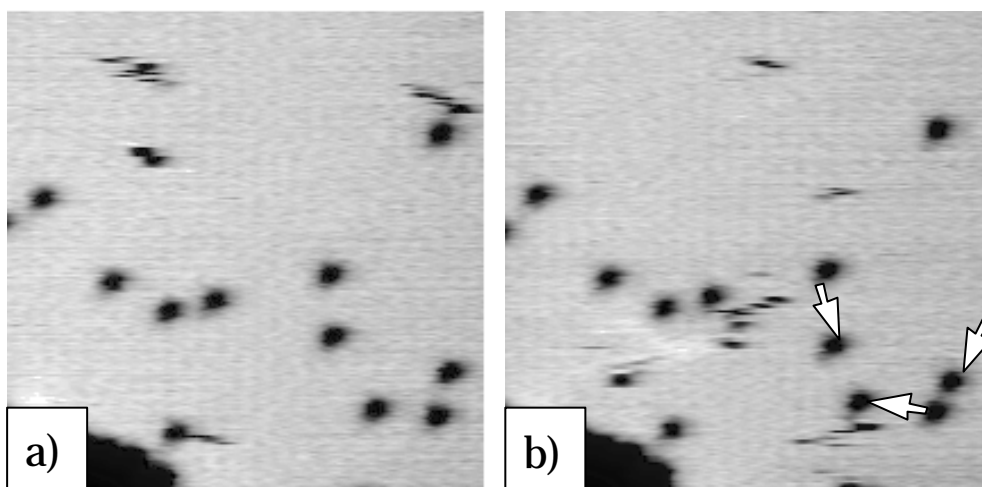


Fig. 5: STM topographs of Ru(0001) recorded after adsorption of 0.1 L NO at 300 K. (a) and (b) were recorded successively on the same area; arrows mark N atoms that have moved between (a) and (b). $70 \text{ \AA} \times 70 \text{ \AA}$, 20.6 V, 1 nA. From Ref. [14], with permission.

Counting the atoms that have not moved yields the probability P that atoms are still found on their original site at time t . If we assume that the jumps are statistically independent (which is surely the case if coverage is low enough), then $P(t) = \exp(-t/\tau)$, where τ is the mean time an ad-atom spends on its adsorption site. The hopping rate h is just the inverse of τ .

By performing the experiment at several different temperatures, it is found, as expected, that the elementary jump rate follows the law of an activated process, i.e.:

$$h = h_0 \exp(-E_d/k_B T) \quad (1)$$

where E_d is the energy barrier the atoms have to surmount in order to jump, and k_B is Boltzmann's constant.

The values of the pre-exponential h_0 and of the energy barrier have now been determined for several systems [12-15]. These accomplishments must be considered as a real breakthrough: having isolated a single elementary step of a surface process, this becomes now amenable of a meaningful comparison between theory and experiment.

Dissociation at steps

Concerning the use of STM in understanding the elementary steps of a catalytic reaction, the last decade or so has witnessed some spectacular results. For example, Zambelli et al. [16] addressed Process

N°1 in Fig. 1a in the case of dissociative chemisorption of NO (a decisive step in the catalytic reduction of nitric oxides), on the (0001) surface of Ruthenium, which is known to be the most selective catalyst.

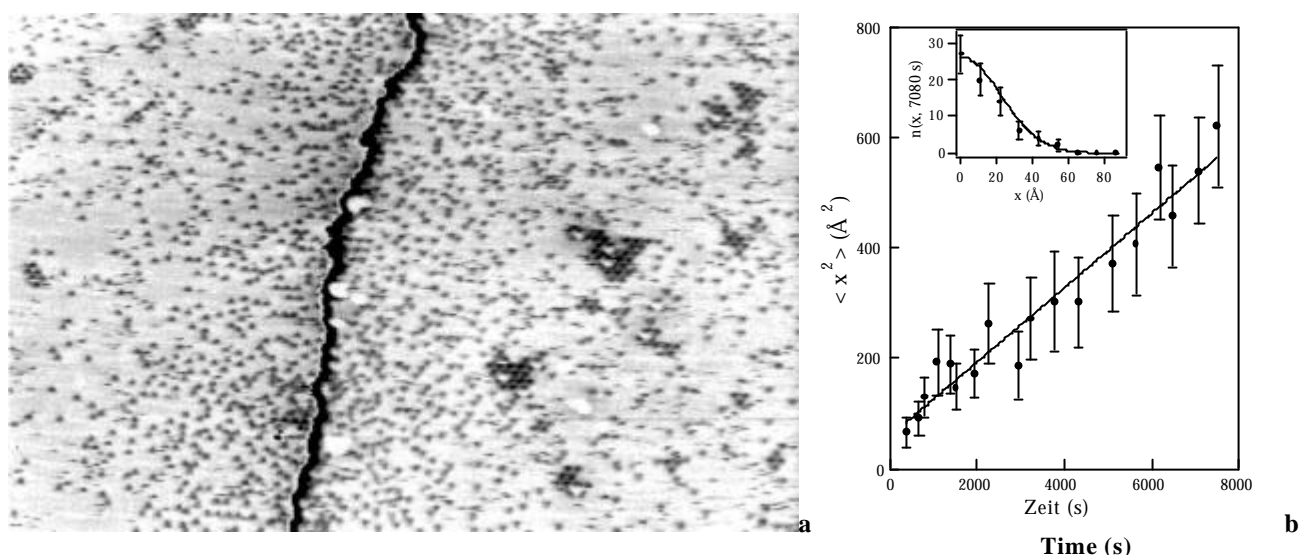


Fig. 5: (a) STM image of a Ru(0001) surface after dissociative adsorption of 0.3 L of NO at 315 K, showing two terraces separated by a monatomic step (black almost vertical stripe). Black dots are N atoms. The concentration profile shows that NO molecules have dissociated at the step. (from Ref. [16], with modifications) (b) Mean square distances of N atoms from the step as a function of time after adsorption. Inset shows the measured distribution of distances at 7080s (points) and a Gaussian with fixed parameters (full line). From Ref. [14], with permission.

The surface was exposed to a small dose of NO (0.3 Langmuir, $1 \text{ L} = 10^6 \text{ torr s}$) at room temperature (RT) and subsequently an STM topography was recorded 0.5 hours after exposure. The results are shown in Fig. 5² above, where a large number of small dark dots is visible on both sides of the step and are identified as N atoms originating from dissociated NO molecules. Small clusters at larger distances from the step are islands of Oxygen atoms³. NO molecules at 300 K and at low coverages are extremely mobile and are not detectable by STM.

The picture which emerges from the distribution of product atoms is quite intriguing: NO molecules, once adsorbed, diffuse rapidly across surface terraces until they meet a step, where they apparently have a very high probability of dissociating. After dissociation, O atoms move rapidly away from steps. Nitrogen atoms also move away but more slowly, so that the image shows a diffusion profile of N atoms with its origin at the step (Fig. 5b).

This experiment clearly shows that Ru(0001) is not uniformly active for the process of dissociation of NO, but rather, that steps are highly preferential sites. The notion of “active sites” on surfaces is an old one in catalysis; however, their exact nature and the mechanism by which they act, have remained elusive for a long time, mainly because of the lack of a local sensitive probe like the STM.

Both sides of the step are covered with a comparable number of N atoms. Observing that N atoms do not cross the step upon dissociation, this means that NO molecules approaching the step, both from the

² The ragged line which crosses the figure almost vertically is a monoatomic step.

³ Identifications were made on the basis of previous experiments with pure N or O layers in which it had been found that O atoms tend to cluster in islands with a (2x2) structure, while N atoms remain randomly distributed [17].

lower and from the upper adjoining terrace, dissociate with approximately the same probability. From this observation Zambelli et al. conclude that the reaction takes place at the frontmost metal atoms at the step.

Besides confirming directly the concept of “active site” in catalysis, this experiment demonstrates that kinetics is influenced by surface structure at sub-nanometer level and confirms that “macroscopic” experiments can only measure an overall reactivity which results from weighted contributions from various surface structure elements at the microscopic level.

Reaction steps

The unequivocal determination of basic mechanisms in catalytic reactions is a long-standing yet elusive goal of research in catalysis. The determination of a set of rate equations which correctly describes the sequence of elementary steps leading to formation of a product is generally hampered by the neglect of one or more intermediate steps and species. The possible existence of parallel branches of a reaction, which may proceed through different mechanisms in different regimes, adds to the complexity of the problem. The identification and characterization of these branches are therefore of high general interest. By combining experimental measurements of Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) it was recently possible to detect two different reaction mechanisms in the catalytic oxidation of carbon monoxide on Rh(110) [18]. The reaction was carried out using a titration experiment. The Rh(110) surface was first exposed to Oxygen until a reconstructed $c(2 \times 8)$ structure was obtained. The surface was then exposed to CO at a selected temperature for a specific time and finally, STM images were acquired. Strikingly different results were obtained after reaction at 160 K and 300 K, suggesting quite different reaction paths and mechanisms in the two cases (Fig.s 6 a and b).

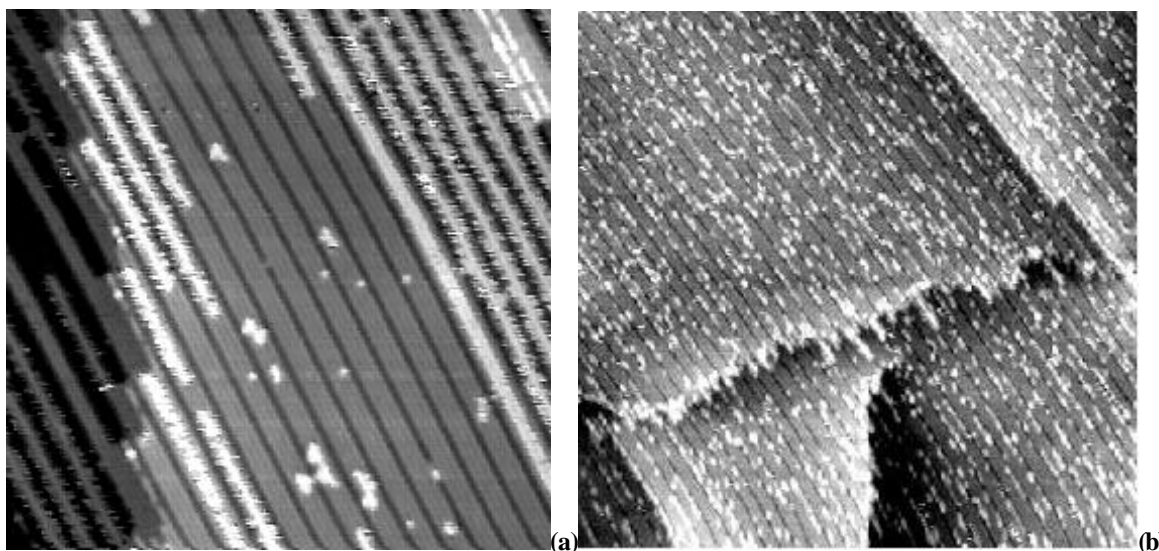


Fig. 6: (a) $34 \times 34 \text{ nm}^2$ STM image of the $c(2 \times 8)$ O/Rh(110) after dosing 2 Langmuir (L) of CO at 300 K. Bright “Christmas garland” lines are reacted stripes occupied by CO. (b) $70 \times 70 \text{ nm}^2$ STM image of the $c(2 \times 8)$ O/Rh(110) after dosing 0.2 L of CO at 160 K. Straight features at top right and lower left are monoatomic steps. From Ref. [18], with permission.

Low temperature STM images showed the reaction starting from centers nucleating uniformly across the surface. At RT instead, the reaction runs in a quasi one-dimensional fashion, along narrow terraces formed by the surface reconstruction. With the help of DFT calculations it was possible to elucidate both reaction mechanisms, and the complex influence of temperature on the overall reaction mechanism.

More complex processes

Surface diffusion becomes significantly more complex at least in two specific cases: when coverage is higher [15] (because molecule-molecule interactions may become significant), and when large molecules are involved.

In a recent, elegant work, Renisch et al. [15] studied the diffusion of O atoms on a Ru(0001) surface. By means of a special fast STM system, they were able to study atoms with very short residence times (down to 10 ms) at RT and to record large data sets within reasonable periods of time. From a statistical analysis of the changes of atom configurations in sequences of more than 1000 images, mean residence times of oxygen atoms in the neighborhood of other oxygen atoms were extracted. The jump distribution was found to be completely isotropic, meaning that it did not show any correlation with the scanning direction. Careful checks for a possible STM tip effect (see next section) revealed that it remained negligible as long as the tunneling resistance did not become too low ($< 1 \text{ M}\Omega$).

The main conclusion drawn from this work was that the residence times under the influence of interactions vary by more than 1 order of magnitude over distances of three lattice constants. This ultimately indicates the need to include the lateral interaction in modeling collective phenomena such as surface diffusion or reactions, even at low coverages.

In a recent letter [19] it was shown that long jumps are the dominant process in the surface diffusion of large organic molecules. In this study, Schunack et al. [19] introduced a new method for determining the root mean square jump length. This method is feasible even if exact displacement distributions are not available or if very long jumps contribute to the diffusion process. The method employs the relation between the diffusion constant, D and the hopping rate, h :

$$D = \lambda^2 h / 2 \quad (2)$$

By plotting $\langle(\Delta x)^2\rangle$ versus ht , it is then possible to determine λ with a reasonable statistical accuracy. This particular topic is discussed in greater detail in another chapter of this book (M. Schunack, F. Rosei, and F. Besenbacher).

Influence of the STM tip in studying diffusion processes

It is well known that besides the normal imaging mode, the STM tip can also be used to manipulate atoms and molecules bound to a surface, in a controlled manner [20-22]. Clearly, when studying adsorbate surface diffusion any influence from the tip must be carefully avoided. This phenomenon was treated theoretically, revealing that besides a direct attractive/repulsive interaction between tip and adsorbate, the tip can actually modulate the potential energy hypersurface, thereby indirectly influencing the diffusion process through the activation energy of the diffusion process itself [23-25].

We will now draw from a recent experiment to show that, by choosing appropriate tunneling parameters it is possible to avoid any influence of the tip on the diffusion process. In particular, we demonstrate that the mean square displacement and the hopping rate of DC and HtBDC molecules⁴ (chosen for the comparative diffusion study described in Ref. [19]) can be made independent of the scanning process. To clarify whether or not the tip influences the diffusion process, displacement distributions were inspected at several different temperatures⁵. Such distributions were always found to be symmetric around a mean value of $\langle\Delta x\rangle = 0.0 \pm 0.8 \text{ \AA}$, indicating that there is no appreciable tip influence [26]. Possible tip-induced artifacts were further investigated by varying the interaction time between molecule and the tip⁶. This was done by either changing the image size and/or acquisition time, resulting in a

⁴ The tip's influence was minimized by scanning with a tunneling resistance above $5 \text{ G}\Omega$ ($V_t=1500 \text{ mV}$, $I_t=0.3 \text{ nA}$) [26].

⁵ The lattice constant of Cu(110) along the [1-10] direction (2.56 \AA) was chosen as bin size for displacement distributions. From high resolution, small-scale images it is known that DC and HtBDC have specific adsorption sites which are spaced in integral multiples of the nearest neighbor lattice distance [26].

⁶ The interaction time is the time necessary for the tip to scan directly over a molecule.

variation of the interaction time [26] between 30% and 300% (compared to regular 500x500 Å² images, which were acquired in ~14 s). No deviation beyond the usual spread around the linear Arrhenius plots was observed. This confirms that there is no influence of the scanning process on the hopping rate or the hopping displacements [26]. Finally, the influence of the tip was investigated directly, by performing controlled STM manipulation experiments. It was impossible to manipulate DC and HtBDC if tunneling resistances above 100 MΩ and 1 GΩ were used, respectively. These values are well below the ones used for imaging. All the results support the conclusion that under the specified experimental conditions, the obtained diffusion parameters are not influenced by the scanning process [26].

Perspectives

One of the problems which has hampered our progress so far, lies in the fact that experimental techniques, for the lack of space or time resolution (or both), usually observe an “ensemble” of different elementary steps and measure therefore parameters which are averaged out over several processes [4, 27]. A great challenge is going to be the possibility of singling out and characterizing every step at the atomic level separately. This will require a substantial improvement of present microscopy techniques and probably, the development of new ones. The effort will be extremely exciting however, since it may also lead to the detection of new important “co-operative” many-body effects of which we had, so far, only occasional glimpses.

Another major obstacle is the so called “pressure gap”. While most model surface science studies carried out so far have used very low pressures (less than about 10⁻⁶ mbar), industrial processes occur at pressures many orders of magnitude higher. Higher pressures mean very high coverage of the reactants. Many experiments have shown that, as the coverage of adsorbed species increases, the lateral interactions which develop strongly influence all surface processes. In this different regime all the elementary steps and the overall reaction rate may change dramatically.

It will be therefore compulsory to improve experimental techniques in order to enable probing surface processes in higher environmental pressures. STM has already shown the capability of performing *in situ* high pressure studies of the atomic structure of surfaces. These first results show that in general, when dealing with the adsorption of a single gas (H₂ on Cu(110) [28, 29], CO on Pt(111), [30]), phases that form at high pressures are also accessible at typical UHV pressures, as long as temperature is kept sufficiently low. This basically means that increasing pressure is equivalent to decreasing temperature, at least in so far as the structure at thermodynamic equilibrium remains kinetically accessible. In the case of CO on Pt(110), which was reported very recently [31], and in which CO adsorption effectively lifts off the (1x2) missing row reconstruction typical of this surface, even though no new phase was reported, it was shown that pressure increase is not quite exactly equivalent to a temperature decrease. In fact at low temperature the rearrangement of substrate Pt atoms would not have the energy required to form the equilibrium structure.

Finally, we refer to recent Transmission Electron Microscopy performed *in situ* on a heterogeneous catalyst [32] with atomic resolution, which have shown that the surface structure of a real catalyst (barium-promoted ruthenium catalyst supported on boron nitride) changes dramatically in the presence or absence of reagents (3:1 mixture of H₂ and N₂, 50 bar). A surface’s response to high pressure therefore appears to be system – specific, and further developments of present experimental techniques will be necessary for a detailed understanding of real catalysts [33].

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