Spatially (nanometer) controlled hydrogenation and oxidation of carbonaceous clusters by the platinum tip of a scanning tunneling microscope operating inside a reactor cell

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Hydrocarbon clusters formed by the thermal decomposition of propylene on Pt(111) were rehydrogenated or oxidized with nanometer spatial resolution using the platinum tip of a scanning tunneling microscope (STM) at 300 K in atmospheric pressures of H_2 or O_2. The reaction rate shows a strong dependence on the oxygen or hydrogen pressures and on the tip–surface separation. The reaction stops when the Pt tip becomes contaminated with carbon, after the removal of $\sim 10^7$–10^8 carbon atoms, but can be regenerated by removing material from the tip by application of a voltage pulse. Dissociative adsorption of H_2 and O_2 on the tip, followed by transfer of atoms to the surface is the proposed mechanism of these tip-catalyzed reactions.

Keywords: catalysis; nanofabrication; STM

1. Introduction

The scanning tunneling microscope (STM) can be used at atmospheric pressures and at various temperatures to provide atomic scale information on the structure of surfaces. For these reasons, STM is a premiere technique for in situ studies of surfaces under catalytic reaction conditions. The technique should be extremely useful in bridging the ten or more orders of magnitude gap that separates traditional surface science studies carried in UHV and the high pressure conditions that prevail in catalytic reactors.

Following this idea, we built a STM operating inside a reaction cell [1]. The usefulness and capabilities of this instrument for novel contributions were already illustrated by the first results, obtained on a model Pt(110) catalyst surface [2,3]. We found that the stable surface structure of this Pt crystal depends strongly on the gas environment. In an atmospheric pressure of hydrogen, the surface exhibits compact rows of Pt atoms in the (110) direction with a variety of multiple and nested missing rows; in 1 atm of O_2, the stable surface is made of facets with (111) orientation; finally, in pure CO, the surface exhibits flat (110) terraces with multiatomic height steps (step bunching). This adsorbate-induced restructuring is likely to occur also in the course of catalytic reactions when the atmospheric gas composition is changing.

The dehydrogenation of propylene on Pt(111) following thermal treatments was also studied in our laboratory with the high pressure STM in various gas environments, temperature and pressure regimes [4]. During the course of this investigation, it was discovered that carbonaceous fragments could be locally (within the spatial resolution of STM) rehydrogenated and removed in the presence of hydrogen [5] or oxygen [6] at atmospheric pressures and at 300 K every time that a clean Pt tip was used.

The purpose of this paper is to report the details of this tip-catalyzed reactions. Specifically we will show how the reaction depends on parameters such as tip composition, tip–surface distance, electric field intensity and polarity, and H_2 and O_2 pressure.

2. Experimental

2.1. *STM reaction chamber*

The apparatus used in these experiments has been described in detail in a previous paper [1] and, therefore, only a brief description is given here. The STM head is housed in a small chamber ($\sim 2\ \ell$) connected to an ion pump and to a detachable turbopump station. An infrared spot lamp located outside the chamber was used to heat the sample through a viewport up to 1400 K in atmospheric pressures. The system was equipped with a quadrupole mass spectrometer which can be differentially pumped for gas analysis while the chamber is pressurized. A turbopumped airlock makes possible in vacuo sample transfer to and from a separate ultra-high vacuum (UHV) chamber.

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2.2. *Sample preparation*

A separate UHV chamber equipped with LEED, Auger spectroscopy, STM and Ar sputtering capabilities was used for sample preparation and characterization [7]. In addition to sputtering, heating in O_2 was used for C cleaning. Before transfer to the high pressure reaction chamber, the clean Pt sample was exposed to H_2S to produce a passivating monolayer of sulfur with a $(\sqrt{3} \times \sqrt{3})R30°$ ordered structure. The sample was then transferred in a cell pumped with a small ion pump down to 10^{-6} Torr pressure. Once in the STM reaction chamber, the protective S layer was removed by heating in pure oxygen at 1 atm pressure.

3. Results

3.1. *Preparation of hydrocarbon clusters*

After removal of the S layer with O_2, the chamber was pumped down to 10^{-5} Torr and a mixture of propylene (10%) and H_2 (90%) (we also used 1–99% mixtures with similar results) was admitted into the chamber with the sample at RT. Propylene readily adsorbs on the surface of Pt under these conditions and forms ordered structures of propylidine ($\equiv C{-}CH_2{-}CH_3$) that have been studied in the past in detail [8–12]. STM images of this surface show flat terraces and monoatomic height steps similar to those seen on the clean Pt(111) surface. No contrast was observed, however, that would indicate the presence of adsorbed propylidyne. This is because, at RT, the mobility of the surface propylidyne species is too high compared with the scanning rate of the STM. A similar effect has been observed by others for adsorbed ethylene [13].

We then decomposed the propylidyne by heating in vacuum (after pumping the propylene–H_2 gas mixture) or after backfilling the cell with 0.1 atm of pure CO. The amount of hydrogen lost from the surface as a result of this heating depends on the temperature. The decomposition of propylidyne produces fragments that undergo polymerization reactions and produce clusters. These larger entities were much less mobile and could then be imaged with the STM. The lowest annealing temperature at which clusters were visible at RT is ~ 470 K, close after the H_2 thermal desorption peak observed in vacuum that signals the decomposition of propylidyne. The bonding of the clusters formed at this temperature to the platinum substrate was weak enough that they could be reversibly displaced on the surface by coadsorbed CO. At temperatures of ~ 550 K, however, they could no longer be displaced by CO.

The clusters have circular shapes and ocupy the entire

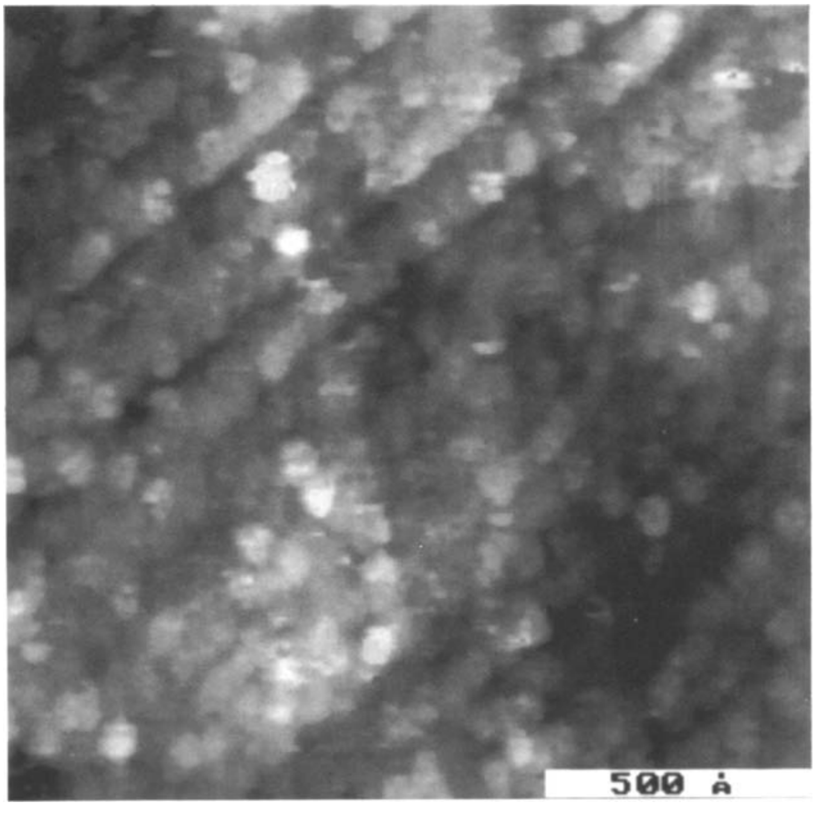


Fig. 1. 1000 × 1000 Å STM image of Pt(1111) (with many atomic steps running in the diagonal direction), after annealing the propylene-covered surface to 550 K in 0.1 atm of CO. Carbonaceous clusters are formed that uniformly cover the surface. The diameter of the cluster is about the same as the terrace width (~ 100 Å). Their height shows a bimodal distribution with 1 and 2 Å.

width of the Pt substrate terraces, forming rows parallel to the step directions, as shown in the example of fig. 1. Only clusters produced by dehydrogenation at temperatures < 650 K were found to be removable by the tip-catalyzed transfer of H and O atoms, as discussed below. A detailed description of the formation, morphology and mobility of the carbonaceous clusters as a function of annealing temperature and gas environment can be found in a recent paper [4].

3.2. *Tip-catalyzed hydrogenation of C clusters*

After producing the carbonaceous clusters by heating in the range of 470–650 K, the cell was pumped and filled again with 1 atm of propylene (1 or 10%) and H_2 (99 or 90%, respectively) mixtures, or with pure H_2, and maintained at RT. We found that when the tip was "activated" by pulses of several tenths of a volt, catalytic removal of the clusters takes place as shown in fig. 2. In the upper third of this image, we observe the clusters that were formed after heating the propylene layer to 550 K, aligned following the direction of the step edges (approximately along the diagonal of this picture). A pulse of 0.9 V was applied at the position marked p that produced bumps ~ 14 Å high. This indicates that material has been transferred from the tip to the substrate. We can see that below this line, as the tip continues to scan, the clusters have been removed. If the tip is immediately moved to a new fresh area while it remains active, all the clusters are removed from the area scanned as shown in fig. 3a. Since the scanning rate is ~ 10^5 Å/s, the hydrogenation rate is of the order of 10^5 carbon atoms/s at 300 K, a very fast rate indeed.

The activity of the tip decayed to zero after some

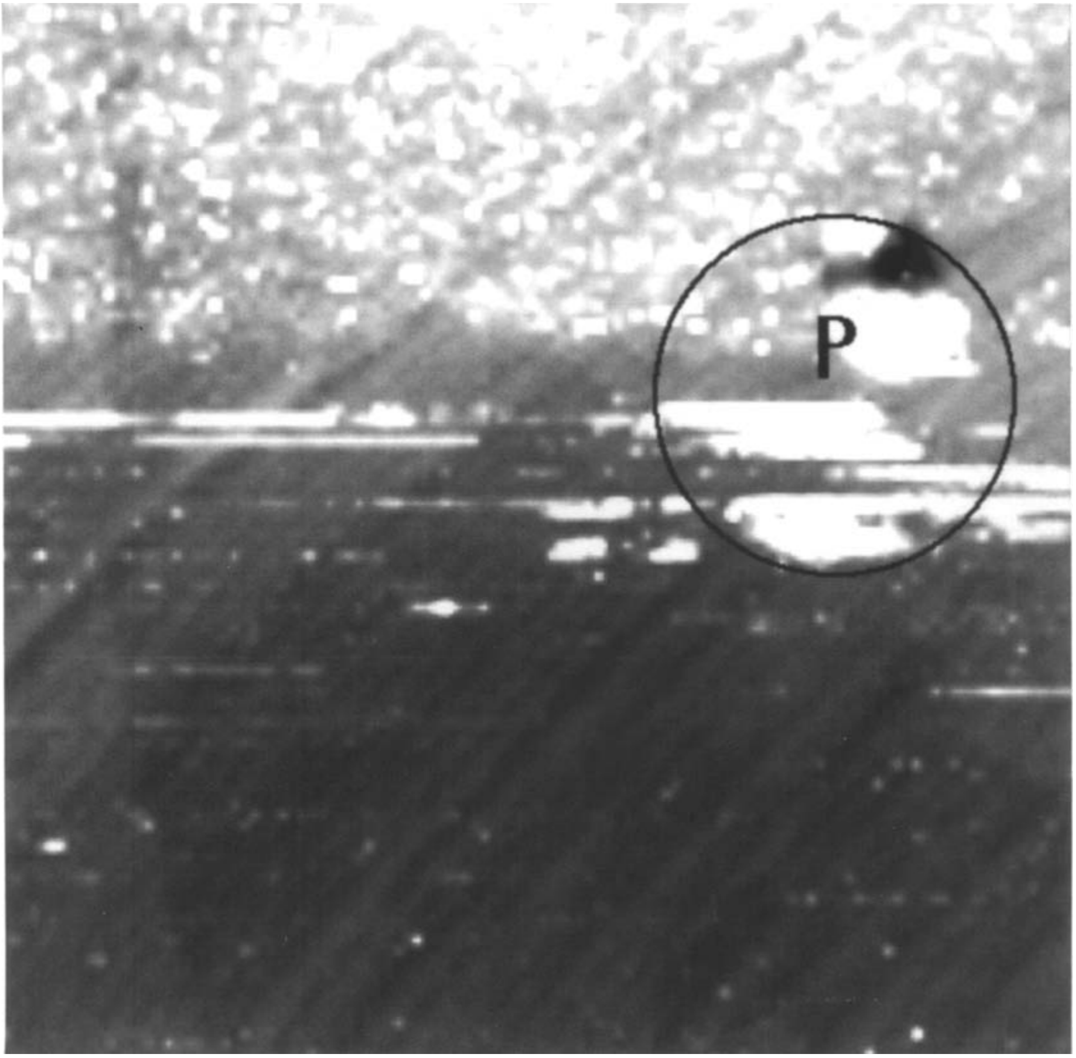


Fig. 2. 3000 × 3000 Å STM image of a surface covered with carbonaceous clusters obtained in 1 atm of a H_2 (90%)–propylene (10%) mixture. The clusters are visible in the upper third of the image. A voltage pulse of 0.9 V was applied to the Pt tip when it reached the position marked, which produced a deposit of material ~ 15 Å high (bright spots next to p). This pulse produced a catalytically active tip that removed all clusters, in the remaining part of the image.

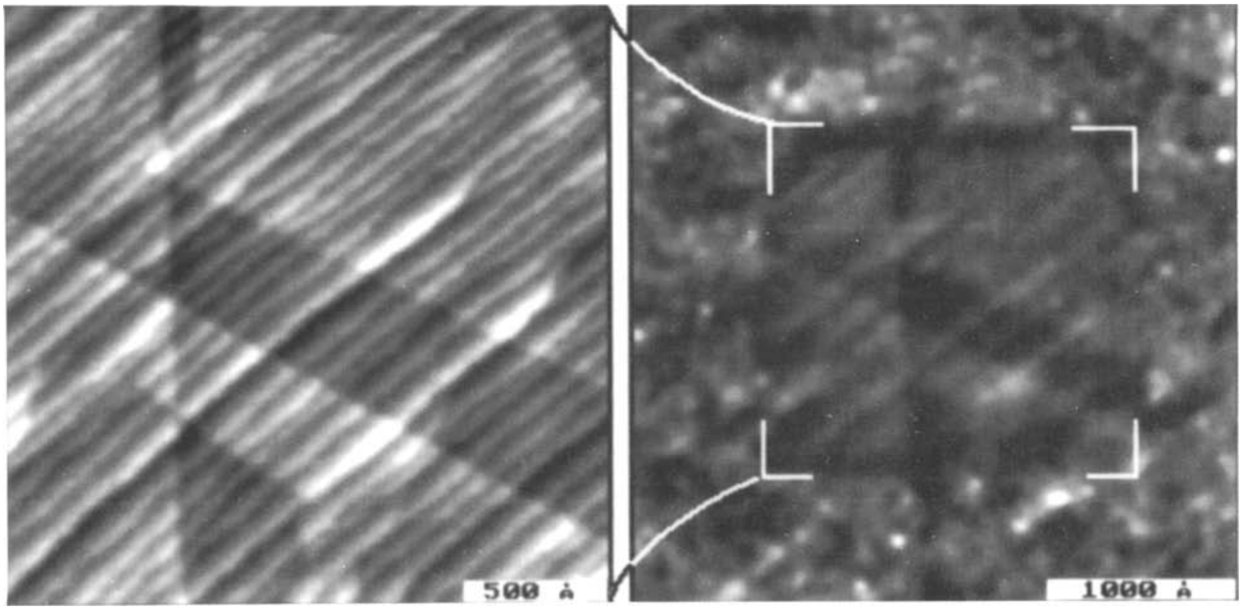


Fig. 3. After activating the tip, a new fresh area was imaged (left), and all clusters were removed so that only the step structure characteristic of the platinum substrate was visible. After a few minutes the tip "deactivated", presumably by contamination, and in this condition the larger image on the right was obtained. The previously scanned area, free of clusters, is visible in the center.

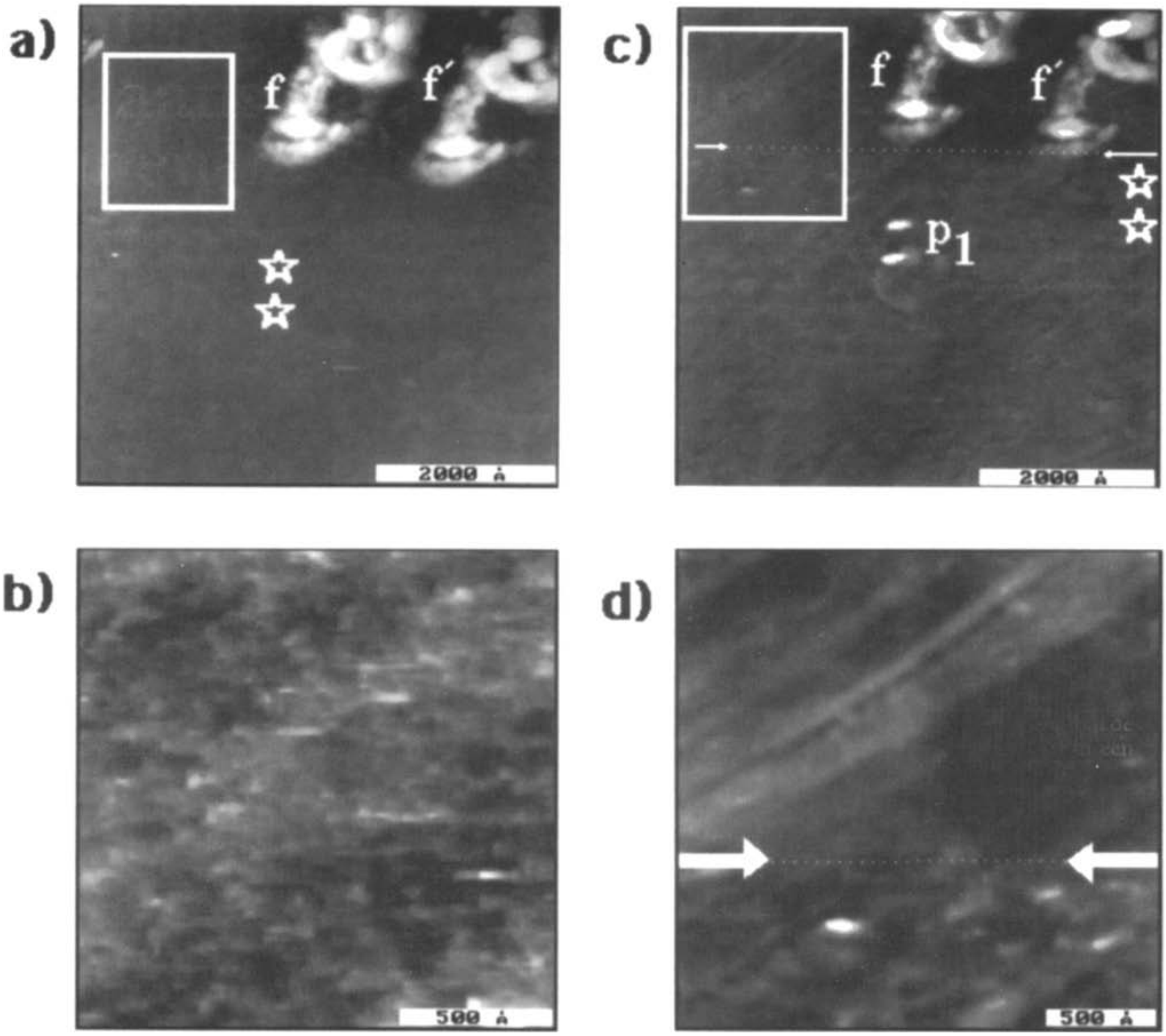
time (on the order of minutes), presumably by contamination which prevented H_2 adsorption and dissociation at the tip. It was in this deactivated state that the image in fig. 3b was obtained. The central square corresponds to the area imaged previously, while the tip was active. Catalytic activity can be readily restored by additional pulses to remove contaminant material, as shown in the sequence of images in fig. 4. The first image (fig. 4a) corresponds to a large area covered by clusters (seen more clearly in the expanded area, fig. 4b), together with a couple of large features in the upper right corner. The two features have identical shape, indicating that they correspond to a single object imaged twice by a double tip apex. The tip was catalytically inactive during the acquisition of this image. Immediately afterwards, the tip was pulsed twice near the center, at the position marked by star signs in fig. 4a. The two bumps in the center of fig. 4c (marked p_1), are the result of the application of these pulses. The activated tip obtained in this way is used to image the same area. As shown in fig. 4c, all the clusters are removed in the top part of the image (see the expanded area in fig. 4d). The large feature is also being thinned out (its height is reduced in half after passage of the active tip), indicating that it is made of hydrocarbon material that is also reacted away by the tip. In this experiment, the tip deactivated at approximately the scan line marked by the arrows and the remainder of the image exhibits the intact original clusters. Another couple of pulses at the positions marked by stars in fig. 4c reactivated the tip once again. In the following scan shown in fig. 4e, all clusters were removed. The large features f and f′ have also been almost completely removed except for a residual core. The bumps from the previous two pulses can clearly be seen at the position marked p_2.

3.3. Tip-catalyzed oxidation of C clusters

In addition to hydrogenation, tip-catalyzed oxidation of hydrocarbon fragments at 300 K was tried with positive results. To carry out the reaction, the cell was filled with 1 atm of pure oxygen. A similar procedure as in the previous case was followed to activate the tip using voltage pulses to remove contamination. Fig. 5 shows an example of these results. The top image shows the surface before tip activation and the bottom one was taken on the same area after activation. Note that not all the hydrocarbon clusters were removed from the scanned region. It is difficult to quantitatively compare the rates of carbon removal by oxidation and hydrogenation because of several other variables that influence the rates, which will be discussed below. It appears, however, that the platinum tips remain active and free of contamination longer in oxygen than in hydrogen or in hydrogen–propylene gas mixtures.

3.4. Failure of gold tips to catalyze hydrogenation and oxidation reactions

When the platinum tip was replaced with a gold tip, the hydrocarbon fragments could not be removed either in hydrogen or in oxygen under the same conditions where the Pt tip readily catalyzes the reaction. We tried various voltage pulses to remove potential contamination from the gold tip with unsuccessful results: we could



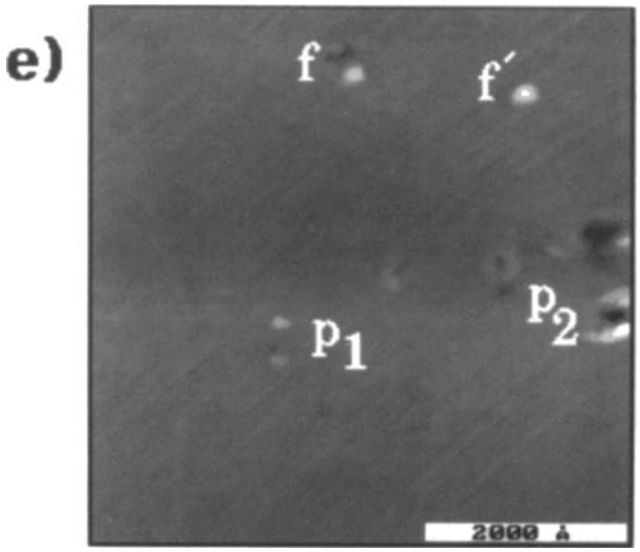


Fig. 4. Activation and deactivation of Pt tips are illustrated in the following images: (a) Large area image (5000 × 5000 Å) obtained with an inactive tip. The surface is covered with clusters, as in fig. 1. The two large features labeled f and f′ in the top right corner correspond to a large aggregate of hydrocarbon fragments that was imaged twice by a double tip. After acquisition of this image, the tip was placed near the center and two pulses of 0.9 V were applied (at the star positions). (b) Enlarged image of the square in (a), showing the clusters. (c) With the activated tip, this new image was acquired. The clusters in the top third were all removed. The large feature f is still visible although its height has been reduced by half. At the line scan position marked by dots and arrows, the tip deactivated, presumably by contamination and no cluster removal occurred thereafter. A magnified image of the square is shown in (d). p_1 marks the position of the bumps left by the previous activating pulses. At the end of the image two new pulses were applied at the position of the stars, on the right hand side. (e) Image obtained after the second pair of pulses. This time the tip remained active over the entire image and all clusters were removed. Feature f is also removed except for a remaining unreactive core. p_2 signals the marks left by the second activating pair of pulses.

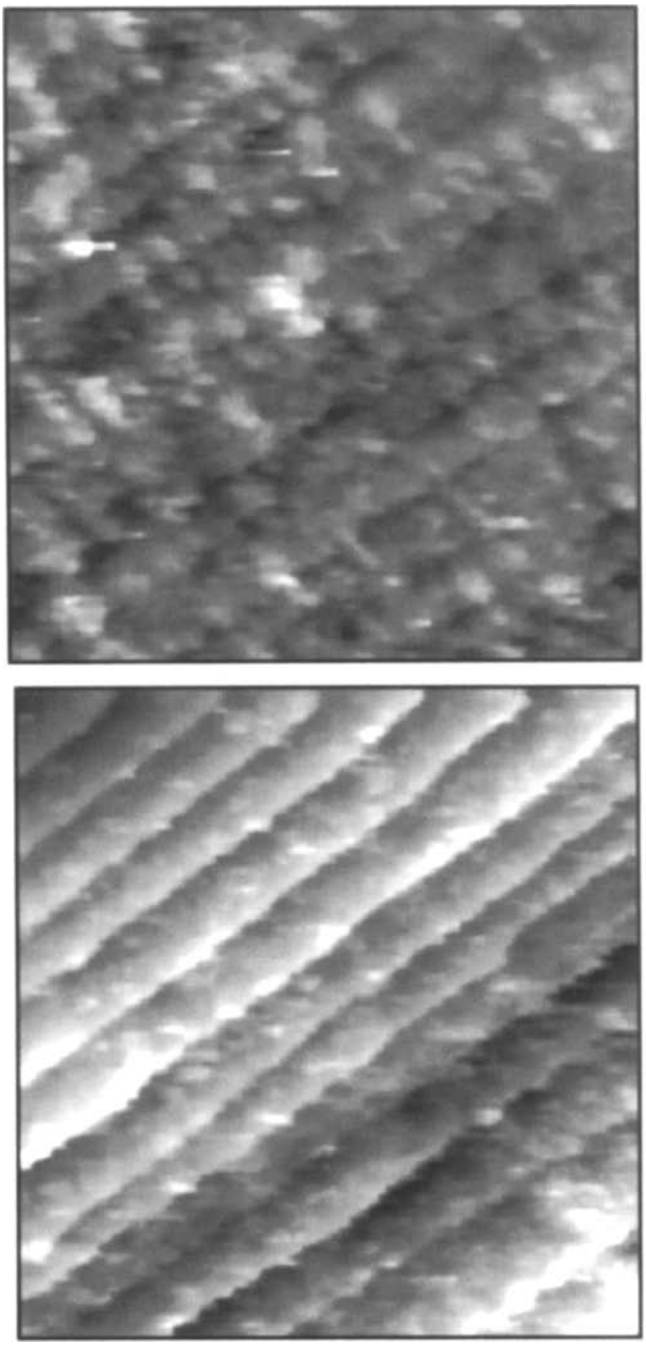


Fig. 5. 1000 × 1000 Å images illustrating the tip-catalyzed removal of clusters in 1 atm of pure O_2. The top image was obtained before activation of the tip, the second one after activation by application of a ~ 1 V pulse.

image the hydrocarbon clusters with the gold tip but no catalytic chemistry occurred.

3.5. *Pressure dependence of Pt-tip-catalyzed reactions*

The next step in our study was to determine the pressure dependence of the tip-catalyzed reactions. The method that we used was to determine the number of scans (which is proportional to the residence time of the tip over the clusters) required to remove ~ 80% of the hydrocarbon clusters from a 500 × 500 Å area, at a given hydrogen or oxygen pressure. We started by using 1 atm of H_2 or O_2, and then we reduced the pressure to lower values. In hydrogen, Pt-tip catalysis stopped (no cluster removal after 20–25 scans) when the pressure was $\leqslant 0.5$ Torr. This can be seen in the series of images in fig. 6 obtained at 0.5 Torr of pure H_2. In these experiments, we also varied the tip–surface separation (by changing the set point value of the tunneling current and/or bias voltage) to see if it affected the reaction rate (we discuss below the dependence on distance and electric field). No catalytic activity was observed under any of these conditions.

In oxygen, we could detect the removal of the clusters at pressures as low as 5×10^{-3} Torr. It appears that the oxidizing environment provides a faster kinetics rate for the Pt-tip-catalyzed gasification at 300 K. This is not surprising as the activation barrier for hydrocarbon oxidation is known to be lower than that of the hydrogenolysis of similar species [14]. A summary of these results is shown in fig. 7. The plot shows that the number of scans necessary to carry the reaction to 80% completion decreases roughly exponentially as a function of gas pressure. This is a rather dramatic pressure dependence, which indicates the importance of using high reactant gas pressures in such a catalytic process.

3.6. *Dependence of reaction rate on the temperature of cluster formation, its size and location*

The higher the temperature that was used to produce the hydrocarbon clusters, the slower its rate of hydrogenation or oxidation. Higher temperatures cause the removal of more hydrogen from the deposit until finally graphitization occurs. When the carbon clusters were produced by heating > 600 K, Pt-tip-catalyzed reactions could not be observed.

Since the hydrocarbon clusters appear to be of two types, with heights of 1 and 2 Å, respectively, that can be readily distinguished by STM, we explored their relative rates of reaction in H_2 and in O_2. Within experimental error, their rates of removal were identical. We could find no reaction rate dependence on the location of the clusters in the terrace either. The clusters were removed with about the same rate from the middle of a terrace or near the bottom or top of a step edge. Fig. 8 illustrates some of these results with clusters prepared by heating to 500 K. In the top images, we see the removal of a cluster on a terrace near a step. In the bottom ones, only the cluster at the bottom of the step was removed in one scan. Eventually they all get removed in a second scan (if the tip remains active). In summary, we found no clear correlation between the ease of cluster removal, their position in the terrace, or their height.

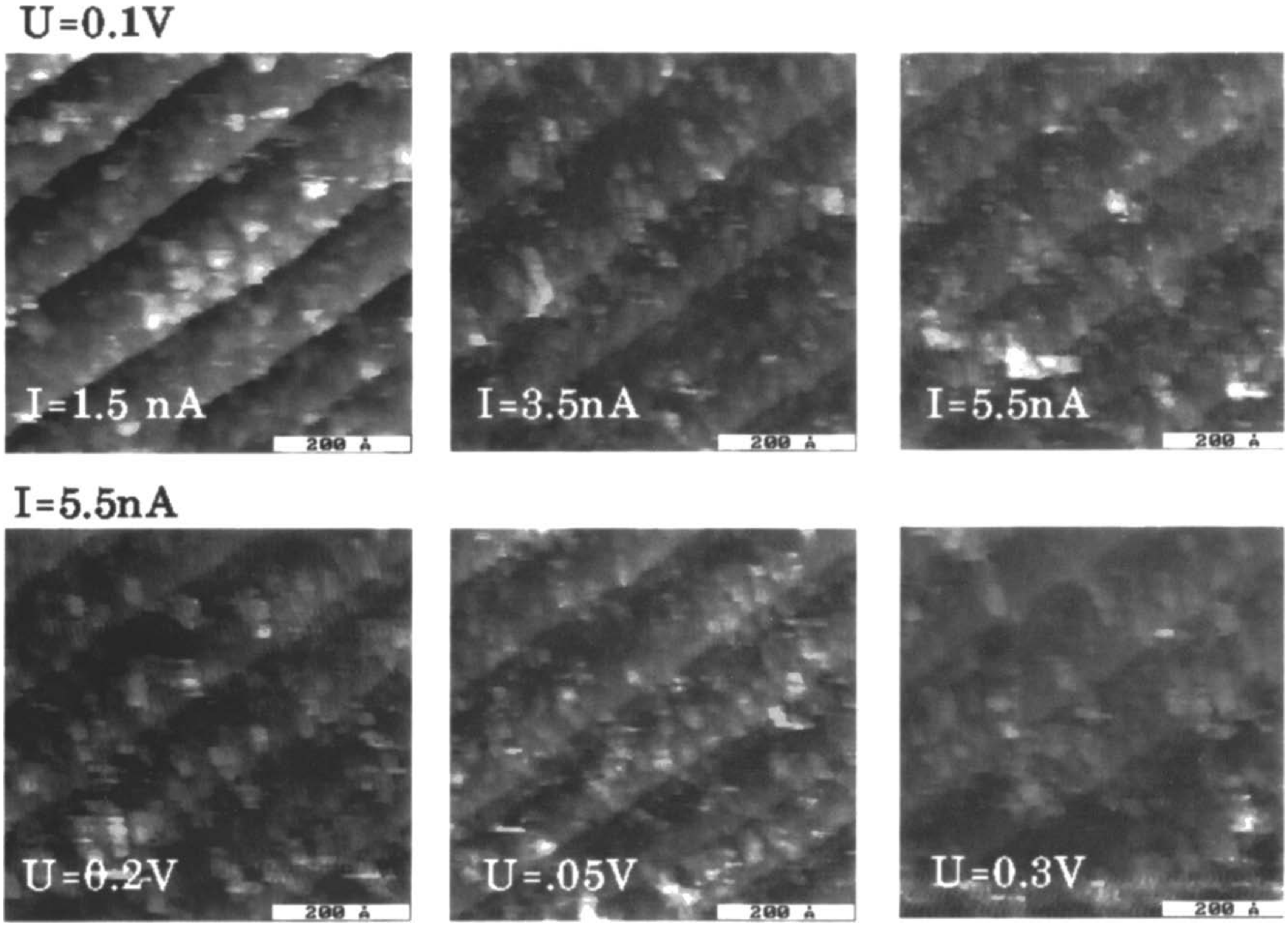


Fig. 6. At 0.5 Torr and lower pressures of pure H_2, the rate of tip-catalyzed rehydrogenation becomes immeasurably small, as illustrated in these images obtained at a variety of tunneling gap resistances and electric fields. No cluster removal is observed at these low pressures.

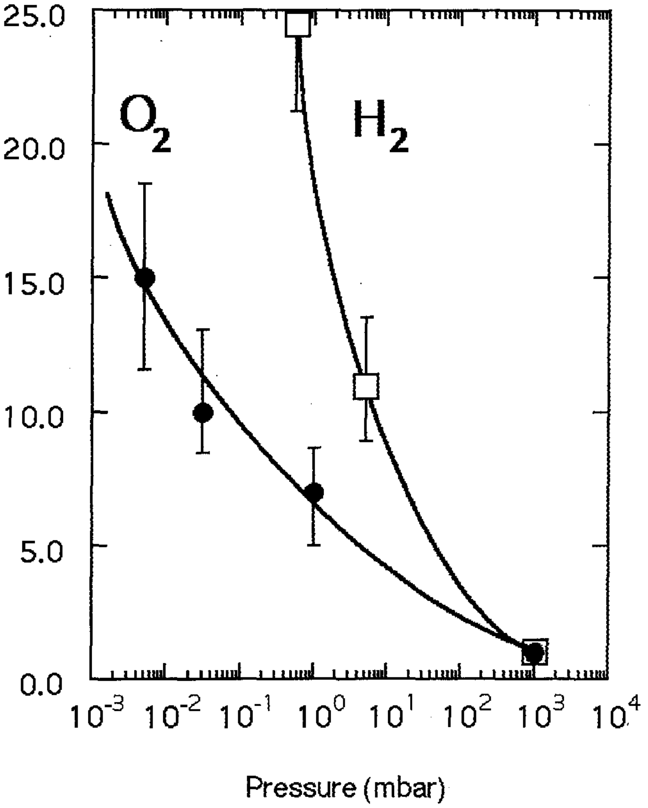


Fig. 7. Semilog plot of the pressure dependence of the tip-catalyzed reactions in H_2 and O_2. The dependence was measured by the number of scans necessary to remove 80% of the clusters. The solid lines through the points are just visual aids.

3.7. Dependence on the tunneling gap parameters

The dependence of the reaction rate on the tunneling gap parameters (current and bias) that affect the tip–surface distance and the role of the intensity and polarity of the electric field between tip and surface were also studied. Fig. 9 shows the effect of decreasing the gap resistance by increasing the tunneling current at a constant bias voltage. The tunneling current, and thus the resistance, depends exponentially on the distance. Therefore, the factor of 3 change in these experiments corresponds to a change in distance of ~ 0.5 Å, assuming a tunneling barrier height of the order of the work function (4–5 eV). As we can see, even this modest approach of the tip has already a measurable influence in the hydrogenation rate.

The effect can be made more visible by changing the gap resistance while STM images are being acquired, as shown in fig. 10. In the top image, scanning was initiated (after activation) with a gap resistance of 350 MΩ. At the point indicated by the arrow, the resistance was dropped to 50 MΩ (corresponding to a change of ~ 1 Å). The removal rate of the carbonaceous clusters was clearly much more efficient. In the bottom image, the gap resistance was varied three times, generating bands of clusters at high gap resistances and "clean" bands in the regions where the tip was scanned at low gap resistance. A very similar effect was observed in oxygen environments as shown in fig. 11. The bottom image in this figure corresponds to a pressure of 5 Torr and shows that, at this pressure, the effect is less pronounced. Thus the tip catalysis is enhanced markedly when the tip is brought closer to the surface, strongly pointing towards a proximity effect.

In the previous experiments, the electric field in the gap changed, in addition to the distance. To separate the two effects and to determine whether electric field effects are significant, we performed experiments in which the gap resistance was kept constant while the tunnel current and bias voltage were increased (or decreased) simultaneously so as to keep their ratio constant. This should keep the tip–surface distance unchanged. No noticeable changes in the reaction rates were observed in these conditions. This was found to be the case in the presence of both hydrogen and oxygen.

Finally, we did not observe any dependence on the sign of the applied bias: both positive and negative tips exhibited similar reaction rates in hydrogen and oxygen.

4. Discussion

The results presented in the last sections clearly demonstrate that the Pt tip of the STM, activated by voltage pulses, is catalyzing the removal of partially dehydrogenated hydrocarbon clusters. Because voltage pulsing to activate the tip produced bumps of material on the surface, we conclude that the activation consists in a cleaning action whereby contaminating layers are field evaporated to expose a clean Pt tip that is capable of dissociatively chemisorbing oxygen and hydrogen. The inactivity of gold tips, even after similar pulsing treatments, supports the idea of a chemically active tip that dissociates the reactant gas phase molecules.

The catalytic nature of the reaction is demonstrated by the large turnover number that can be estimated from our data. Since the residence time of the tip over the area occupied by one cluster is on the order of milliseconds at our scanning speeds, the frequency of the H transfer reaction from the tip is ~ 2 × 10^3 per Pt site per second. A similar number is obtained for the oxidation reaction. This is about one order of magnitude higher than that expected from comparable reactions, such as the hydrogenation of ethylene or propylene under similar conditions [15] and several orders of magnitude higher than hydrogenolysis reactions [16]. This is not surprising, however, because here it is not necessary for the molecules to be completely rehydrogenated to be unobservable in the STM images.

We propose a direct transfer of atomic H or O from the tip to the surface as the basic mechanism of the tip catalysis activity. We can dismiss any mechanical action

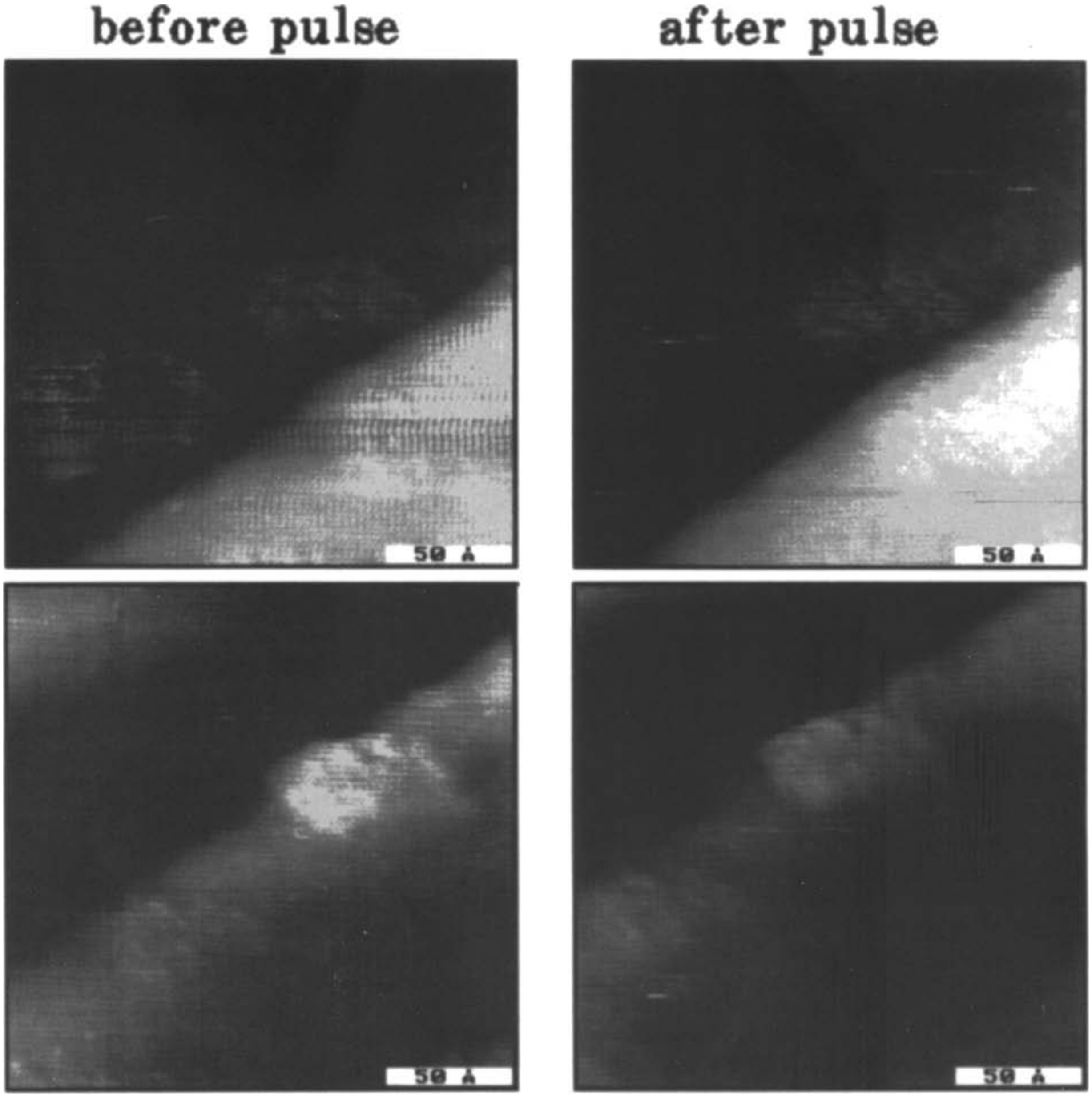


Fig. 8. Images taken before and after tip activation (left and right, respectively), showing the removal of single clusters in 1 atm of H_2. In the top images, we see the removal of a cluster in the terrace near a step. The second cluster, nearest to the step, was not removed in this scan. The bottom images show the removal of the cluster at the bottom of the step while the other cluster at the top remained. A study like this revealed no clear preference for cluster removal as a function of size or location on the surface.

where the tip would be pushing and displacing the adsorbates outside the scanned area. Such mechanical effects have indeed been observed in other instances, particularly when tips contaminated by insulating layers are used [17,18]. In our case, however, piled-up material at the boundaries of the scanned area was never observed, even after re-imaging with larger scans and at high gap resistances. Neither could we observe such mechanical displacement when using inactive platinum or gold tips at similar gap resistances. Finally, this is ruled out by the need to use hydrogen or oxygen background pressures to observe the effect. As described previously, no removal of clusters occurred when CO or vacuum environments were used.

While the precise mechanism of the atom transfer is not clear, some processes can be eliminated. For example, the transfer of atoms is not field enhanced, at least in the regime explored here ($\sim 10^6$ V/cm). However, fields that exceed this value by one order of magnitude can result in the emission of material from the tip, as seen in the activation experiments by voltage pulses. Field evaporation of H from Pt tips onto Si(111) at high bias (3.5 V) has also been observed [19]. We propose a close proximity effect since only at close distances of separation (within 1 Å) did the catalytic effect take place. In this model, transfer occurs when the tip is at about the van der Waals distance from the surface, as depicted in fig. 12. It is likely that this transfer is a thermally acti-

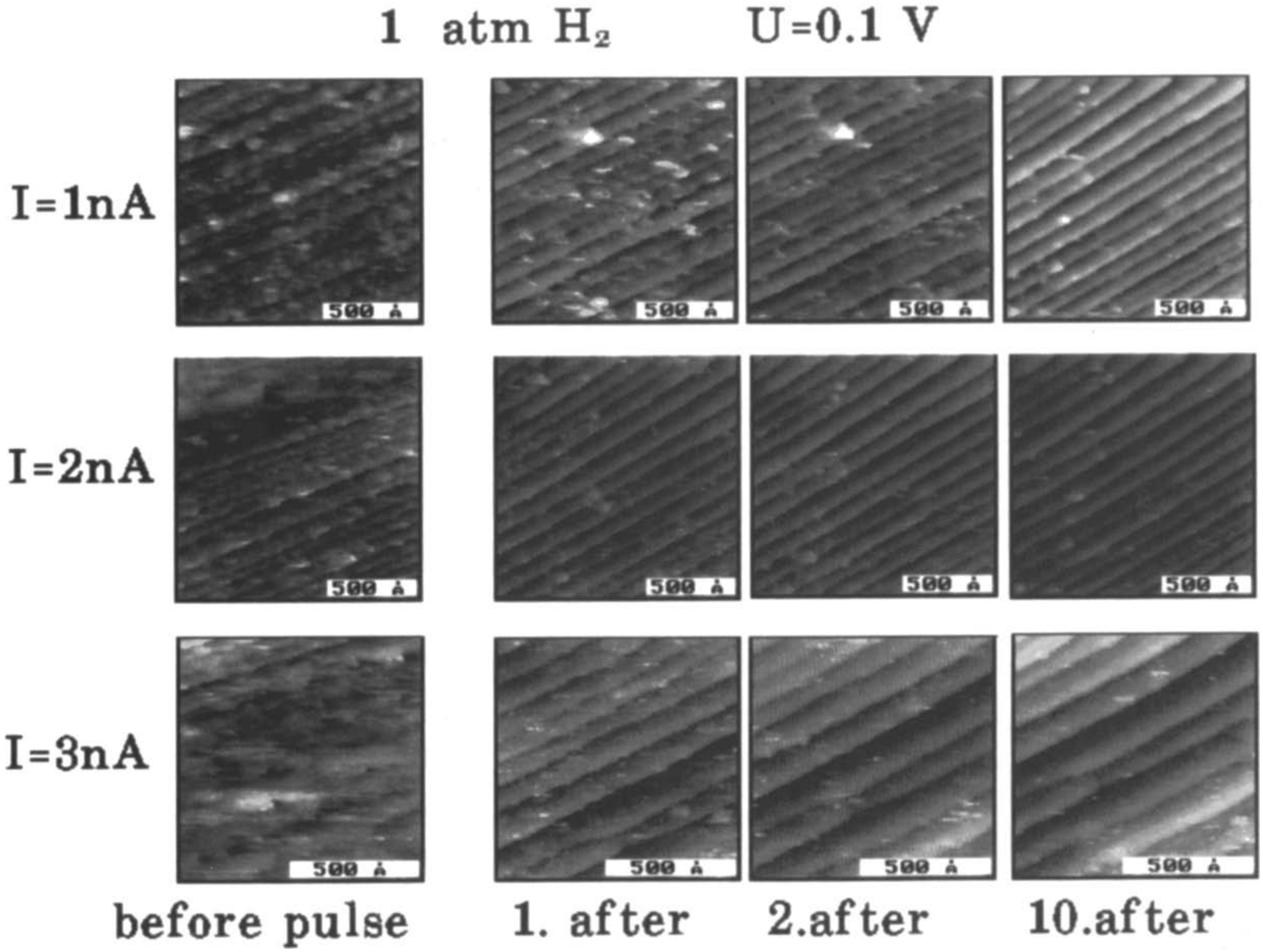


Fig. 9. Images showing the dependence of the tip-catalyzed hydrogenation as a function of tunneling gap. The images on the left were taken at different areas before tip activation. The sequence at the right correspond to the first, second and tenth scan after tip activation. The removal rate is higher for the smaller gaps (last row, for 3 nA current).

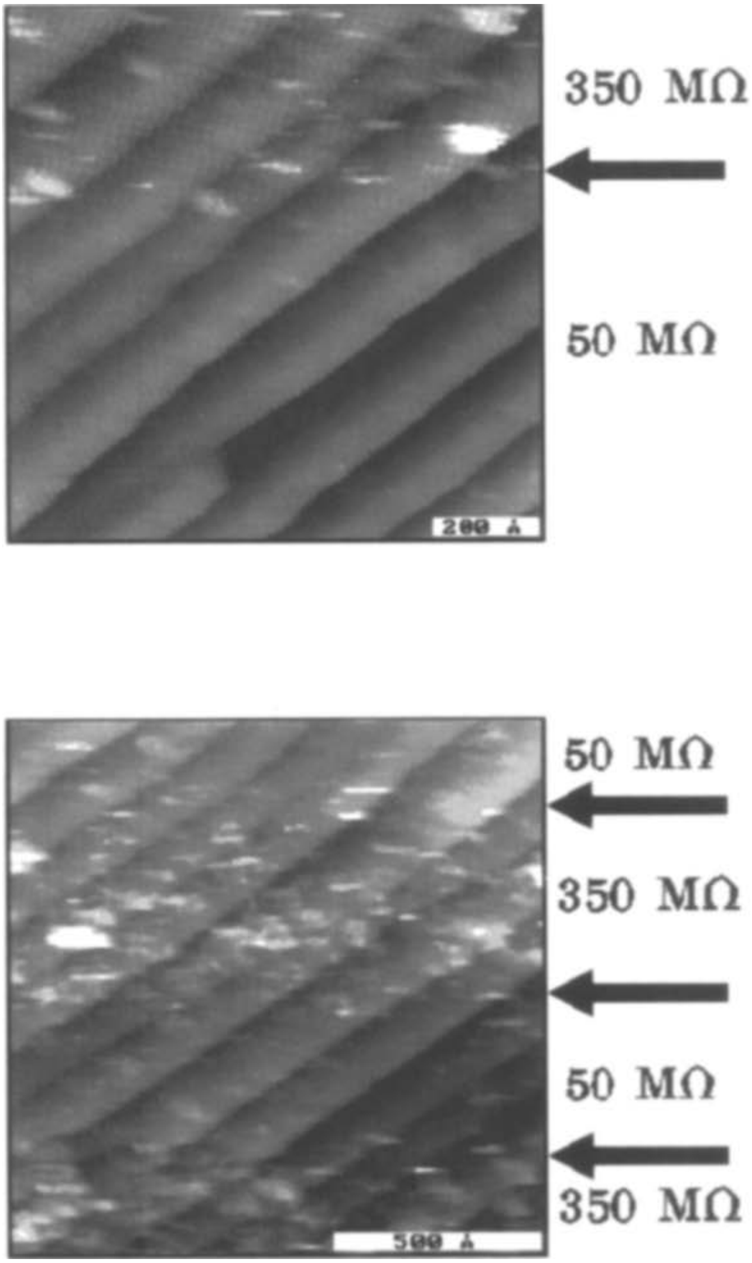
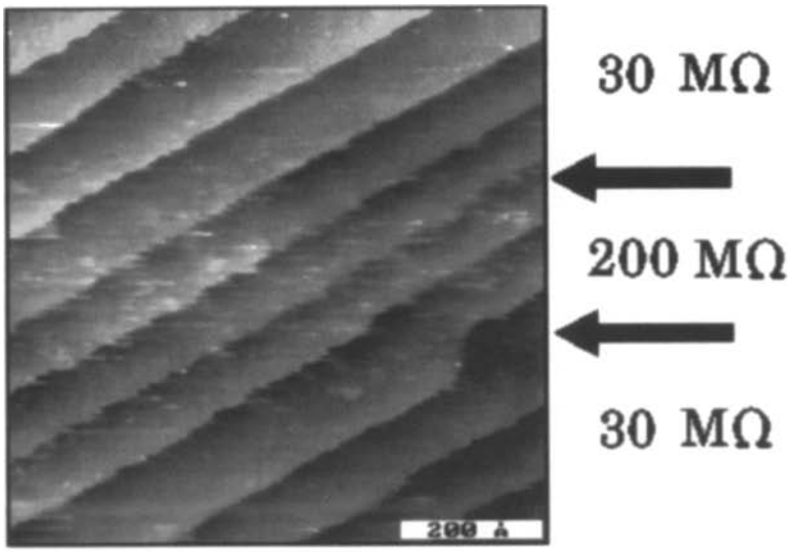


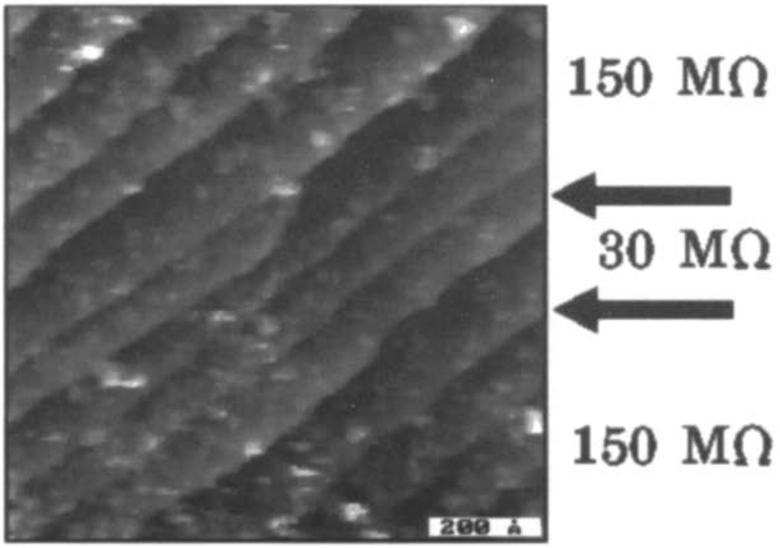
Fig. 10. Images showing the changes in rehydrogenation reaction rate in one image as the gap resistance is changed back and forth from 350 and 50 MΩ in 1 atm of H_2. This corresponds to roughly 1 Å change in tip–surface distance. Each image is taken on different areas of the surface after tip activation.

vated process of crossing a barrier between two chemisorption sites on each side of the gap. Tunneling of atoms through this barrier seems unlikely in view of the similar rates (within one order of magnitude) observed for H and O transfer. Their large mass difference should strongly favor tunneling of H, which is not the case. Unfortunately, our results on the distance dependence of the reaction rate are not sufficiently accurate at present to justify a more detailed analysis at this time.

Another question that is not completely resolved is whether the H or O atoms are transferred directly to the C-clusters or adsorb first in nearby substrate sites from where they are added to the cluster. In view of the fact that no cluster removal occurred by simple exposure to the hydrogen or oxygen background, we lean towards direct transfer to the adsorbed species as the leading mechanism. The nature of the reaction products is not clear at present. Either the hydrogenated species split into smaller units (hydrogenolysis), such as light alkanes or alkenes that rapidly diffuse and become invisible to



1 atm O_2



5 torr O_2

Fig. 11. Images showing changes in cluster removal rate by the Pt tip, in oxygen environments as a function of gap resistance. As in the previous figure, the gap was changed at the position marked by the arrows. In the bottom image, obtained at 5 Torr of O_2, the changes are less dramatic than at 1 atm, as in the top image.

the STM, or the hydrogenated (oxygenated) species desorb into the gas phase. Due to the minute amount of desorbed material, it would be a very difficult task to detect this species in the gas phase at one atmosphere.

The exponential dependence on the pressure cannot be associated with any particular adsorption/reaction mechanism since, due to the limited volume between the tip and surface and the "shadowing" effect of the tip, the limitation is mostly likely due to the hindered arrival of gas phase species to the clean apex of the tip.

5. Conclusions

The observations presented here constitute the first evidence of a catalyst of nanometer-scale dimensions that can be used to perform surface reactions with near atomic spatial resolution. It could lead to new applications of heterogeneous catalysis. Undesirable contaminants could be removed from active sites, thereby permitting regeneration of catalysts on the atomic scale and identification of the true reaction site. Functional

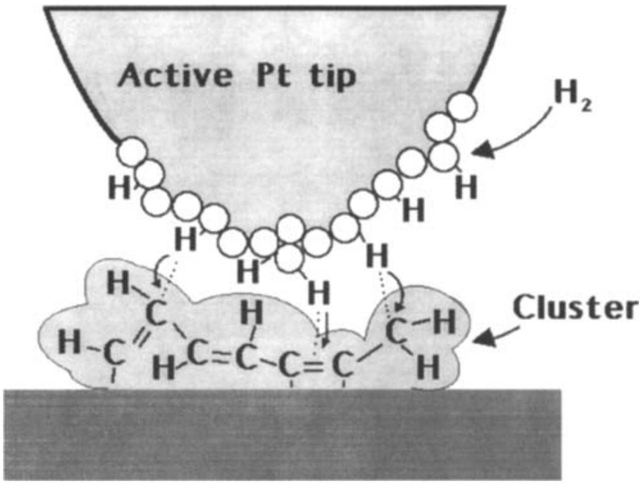


Fig. 12. Schematic drawing illustrating the proposed model for tip-catalyzed reactions of hydrocarbon clusters. The active tip dissociatively chemisorbs H_2 and O_2 molecules from the gas phase. At close proximity, presumably within van der Waals separation, the atoms can jump to the cluster and break C–C bonds in hydrogenolysis or oxidation reactions. The clusters dissociate into small fragments that either remain on the surface and move very fast (eluding imaging by the tip) or desorb into the gas phase, depending on the degree of hydrogenation or oxidation.

groups on molecules may be oxidized or hydrogenated without altering the rest of the molecule. Nanometer-size metallic or oxide deposits could be produced by platinum STM tip catalysis. Studies are under way in our laboratory to further explore Pt-tip-catalyzed chemical processes.

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