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Formation and Morphology of Hydrocarbon Clusters on Pt(111) Produced by the Thermal Decomposition (Coking) of Propylene under High Pressures of H_2 and CO Observed *in Situ* by Scanning Tunneling Microscopy

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A scanning tunneling microscope that operates inside an atmospheric pressure chemical reactor cell has been used to study the structure of a Pt(111) model catalyst surface during the thermal decomposition of propylene (coking). Carbonaceous clusters were produced by partial dehydrogenation and polymerization of the hydrocarbon. Flat (1 and 2 Å high) clusters formed with lateral dimensions of several tens of angstroms. The clusters were found to be mobile when the degree of dehydrogenation was low but became immobile with more extensive dehydrogenation. The amount of dehydrogenation and the structure of the hydrocarbon cluster depended upon annealing temperature (in the range from 300 to 800 K) and gas environment (vacuum, CO, H_2/propylene).

INTRODUCTION

The decomposition of organic molecules on metal catalyst surfaces during hydrocarbon conversion reactions is commonly called coking in the literature (1–3). The presence of stagnant carbonaceous deposits that cover platinum catalysts for many turnovers is well documented and it has been reported that the concentration of this deposit increases with decreasing hydrogen-to-hydrocarbon ratio that is employed during the catalytic reactions and also with increasing reaction temperature. The hydrogen content of the carbonaceous deposit also decreases with increasing temperature, leading to graphitization and poisoning of the catalyst (4–6).

Light alkenes (ethylene, propylene, 1-butene) have often been used in hydrogenation–dehydrogenation reactions in surface science and catalysis studies (7–20). Studies performed in ultra-high-vacuum environments revealed that, at temperatures up to 250 K, the alkenes adsorb with the C=C bond axis parallel to the Pt(111) surface. At temperatures above 250 K, they convert irreversibly to ethylidyne (C_2H_3), propylidyne (C_3H_5), and butylidyne (C_4H_7) by loss of hydrogen. Scanning tunneling microscopy (STM) has also been used to study the dehydrogenation processes for ethylidyne on Pt(111) in ultra-high vacuum (21). It was observed that, upon heating to 500 K, the surface was uniformly covered with carbonaceous particles ∼10–15 Å in diameter. Annealing to higher temperatures resulted in the formation of graphite islands which eventually accumulate at the Pt steps and inhibits the motion of step atoms.

The propylidyne species is stable in vacuum up to 400 K. Above that temperature, it undergoes C–C bond scission and loss of hydrogen, forming fragments that include ethylidyne and methylidyne species. In thermal-programmed desorption (TPD) experiments, the maximum H_2 desorption rate from this decomposition reaction occurs at 435 K (17). Above 500 K, more hydrogen is lost and the surface is characterized as having carbonaceous species of CH (methylidyne) and C_2H (acetylide) stoichiometry. Above 550 K, the surface hydrocarbons appear to aggregate and form large clusters, as shown by STM studies reported in this paper. Above 800 K, the dehydrogenation is complete and the carbon clusters form graphite. Figure 1 summarizes the structural changes that occur upon the adsorption and decomposition of propylene on Pt(111) in vacuum.

STM is an excellent technique for investigating the shape, structure, and mobility of the carbonaceous fragments on the molecular scale. In addition, STM can operate under a wide variety of experimental conditions of hydrocarbon and hydrogen pressures. We built a high-pressure scanning tunneling microscope (HPSTM) that can monitor the surface structure during reactions as well as other ambients (22, 23).

In this paper we report on the decomposition of propylene on the Pt(111) crystal surface as a function of temperature in the range of 300–800 K in a variety of environments: in the presence of hydrogen, in carbon monoxide, and in

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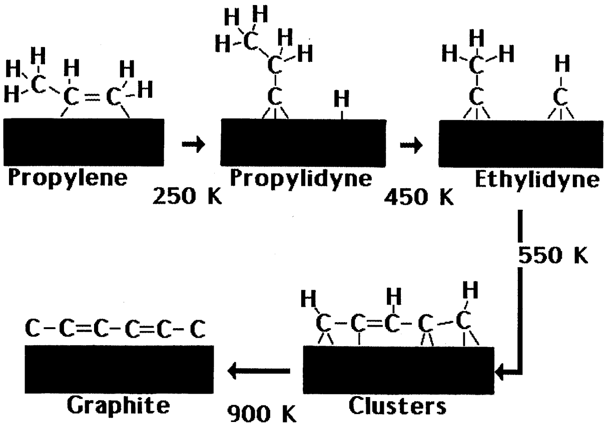

FIG. 1. Schematic diagram of the thermal decomposition of propylene on Pt(111) in UHV, as determined by HREELS and LEED studies. At temperatures up to 200 K, propylene absorbs intact with the C=C bond axis parallel to the Pt(111) surface. At temperatures >200 K, propylene converts irreversibly to propylidyne by a loss of hydrogen. The Pt_3–C–C bond axis is perpendicular to the surface. The propylidyne species undergoes C–C bond scission and further loss of hydrogen-forming ethylidyne and carbonyl species at temperatures >450 K. Above 550 K, the surface hydrocarbons appear to form clusters having wide-ranging stoichiometries. Cluster formation occurs at temperatures as low as 475 K in CO environments. Above 900 K, the carbonaceous species form graphite.

ultra-high vacuum. STM studies show that, under conditions of propylene hydrogenation at 1 atm in 9 : 1 H_2-to-propylene ratio, the average step structure of the Pt(111) surface remains unchanged. These findings are in contrast with the massive restructuring of the less stable Pt(110) surface, which undergoes faceting in O_2 atmospheric pressures, and multiple step coalescence in CO atmospheres (24). There is no formation of stable hydrocarbon clusters until at temperatures above 700 K in this circumstance, while in hydrogen-lean environments (UHV or CO), they form at temperatures between 450 and 550 K. The morphology of the carbonaceous deposits is also different, depending on the gas ambient and temperature. There is evidence for their mobility at 475 K and for their lack of mobility at 600 K. The organic fragments cause step restructuring in the Pt(111) surface as the temperature is increased. It appears that HPSTM is an outstanding technique for studies of catalyst coking.

EXPERIMENTAL

The experiments were carried out in two chambers. A UHV chamber equipped with LEED, Auger, and STM was used for sample preparation, including Ar sputtering and heating in O_2 for C cleaning and for decomposition studies in high vacuum. 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 $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered structure. The sample was then transferred in a small cell pumped with a small ion pump at 10^{-6} Torr. Details of the STM high-pressure chamber are described in recent publications (22, 23). Once in this chamber, the protective S layer was removed by heating in a pure oxygen pressure of 1 atm. A focused infrared-spot heater was used to anneal the surface while in atmospheric pressures of gases.

RESULTS

Ultra-high Vacuum STM Studies

STM images of the clean Pt(111) surface and after the chemisorption of propylene at 300 K show straight monatomic-height steps with ∼150 Å terrace widths (Fig. 2). The direction of the steps due to miscut of the crystal is, on average, 15° off a compact direction of the $[1\bar{1}0]$ type. This can be seen in images such as in Fig. 4A. The propylene-covered surface was obtained by exposing the initially clean surface to ∼110 L of pure propylene. This exposure is known to produce a saturation coverage of 0.25 monolayers (18) of propylidyne. The individual propylidyne molecules were not resolved by STM at room temperature, presumably due to their high mobility, as found also in previous STM studies of ethylidyne at room temperature (21).

Annealing the propylidyne-covered surface to temperatures <550 K did not produce noticeable changes in the step structure and no clusters were visible. Images showing clusters were only obtained when the temperature reached ∼550–600 K and beyond. Since the TPD results indicate that decomposition reactions take place at and above 435 K, we must conclude that the C fragments that are produced are small and mobile to elude imaging by the STM.

Annealing at 800 K nearly completely dehydrogenates the organic monolayer and leaves carbon residues that form particles 30–50 Å in diameter and 1–2 Å in height more or less uniformly distributed over the surface, as shown in Fig. 3. These particles appear to be slightly larger in average diameter than the clusters observed by Land *et al.* after they employed similar annealing temperatures for ethylidyne (21). The clusters have a bimodal height distribution, with values of ∼2.3 Å for the taller ones and ∼1.2 Å for the shorter ones. This could indicate that the clusters are one or two carbon atoms high. A similar cluster height distribution was observed when annealing in CO environments (see below).

It is also apparent that, after annealing, the steps are no longer straight. The images show that there is particle growth at the step edges, which causes pinning of the steps, resulting in increased surface kink densities (step roughening). From the shape of the steps around the pinning particles (Fig. 3), it appears that the step edges receded during the 800 K annealing. It is interesting to note that Land *et al.* did not observe step pinning until after annealing to 1200 K (21). This temperature is well above the temperature

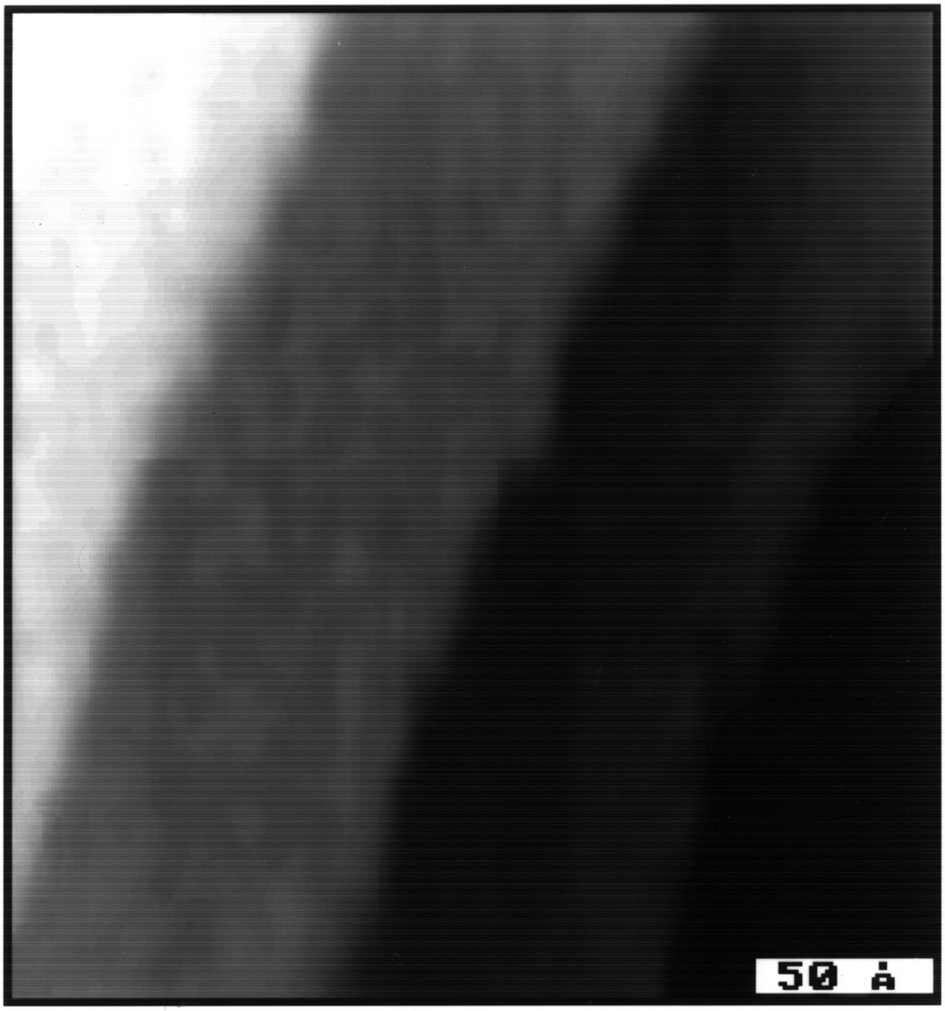

FIG. 2. STM image of the Pt(111) surface at room temperature when covered by propylene. The images show approximately straight, monatomic-height steps with ∼150 Å terrace widths. The propylidyne molecules are too mobile at room temperature to be resolved with the relatively slow-scanning STM tip.

required for the formation of graphite. It may be that the lower temperature step pinning observed in this work occurred because the Pt(111) surface that we use has a significantly higher step density and therefore, higher surface energy leading to faster kinetics of carbon-induced step restructuring.

Decomposition of Propylene under Catalytic Reaction Conditions

After removing the protective S layer by heating in 1 atm of O_2, the reactor cell was pumped down to 10^{-5} Torr and a 1-atm mixture of propylene (10%) and H_2 (90%) was admitted to the chamber with the sample at 300 K. It should be noted that, under these conditions, the Pt surface is active in catalyzing the hydrogenation of propylene to propane (25).

The STM images show the surface consisting of flat terraces and monatomic height steps that are characteristic of the initially clean Pt(111) surface (Fig. 4). No atomic resolution was obtained, however, again as a result probably of the rapid mobility of the propylidyne and other possible small fragments. It is important to note that no change of Pt step morphology takes place during reaction conditions at 300 K.

We proceeded to heat the surface in the hydrocarbon/hydrogen atmosphere using the infrared spot heater. We found that carbonaceous clusters did not form until after heating to 700 K. This is ∼150 K higher temperature than necessary to form carbonaceous clusters in vacuum and ∼250 K higher than in CO environments, as discussed below. This indicates that the dehydrogenation/polymerization reactions are inhibited by the presence of atmospheric pressures of hydrogen. This is likely due to the efficient rehydrogenation of any fragmentation product to more saturated and mobile hydrocarbons, such as propylene and ethylene, or to fully hydrogenated propane, ethane, and methane, that desorb to the gas phase.

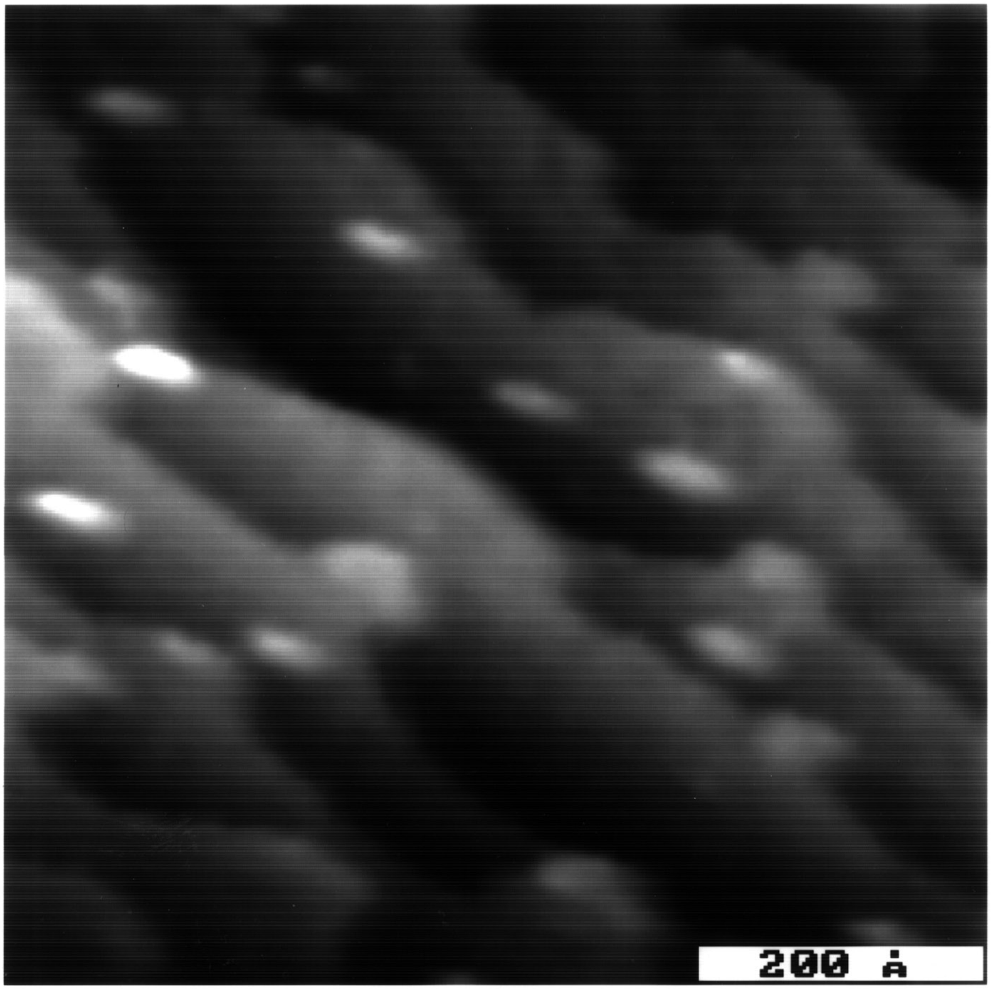

FIG. 3. STM image in UHV after annealing the propylene-covered surface to 800 K. Carbonaceous clusters of ∼30–50 Å in diameter are observed uniformly distributed over the surface. Many of the clusters are attached at the step edges and produce step pinning.

Methane desorption has indeed been detected by IR under these conditions (26). A very different behavior is observed in pure H_2. Clusters do not form in this environment at least until >900 K, due to rapid hydrogenation of any C residues, including those produced by heating first in pure CO environments at 800 K (see below).

Figure 5 was taken after heating the surface to 800 K in the presence of a 90% hydrogen/10% propylene mixture. These images show 20–30 Å particles forming elongated aggregates (200 Å × 75 Å). The diagonal lines running across the images are monatomic height steps. The elongated nature of the aggregates is not understood, but could be due to coadsorbate (hydrogen and/or propylene) interactions, which force the hydrocarbons to the edges of adsorbate islands.

Decomposition of Propylene in Carbon Monoxide

There are several important differences between the hydrocarbon clusters that form during coking in UHV and in the high-pressure experiments. Rehydrogenation reactions retard the formation of clusters that form by the polymerization of the decomposition fragments. There is also blocking of Pt sites by the adsorbed H and by the hydrocarbon fragments. To study the effects of site blocking that should be particularly important at high pressures of reactant gases, we studied the thermal evolution of the hydrocarbon-covered surface in the presence of CO, a readily adsorbed and yet unreactive gas.

Following the same preparation described in the experimental section, the Pt sample was exposed to the atmospheric pressure of the 9 : 1 propylene/H_2 mixture at room temperature that generates the saturated propylidyne monolayer. Then the chamber was pumped down and the cell was backfilled with pure carbon monoxide up to a pressure of ∼0.1 atm. The carbon monoxide was prepurified by leaking in only the vapor from a liquid nitrogen-cooled manifold which contained an activated charcoal filter. This was done to prevent the introduction of iron carbonyls from the gas cylinder.

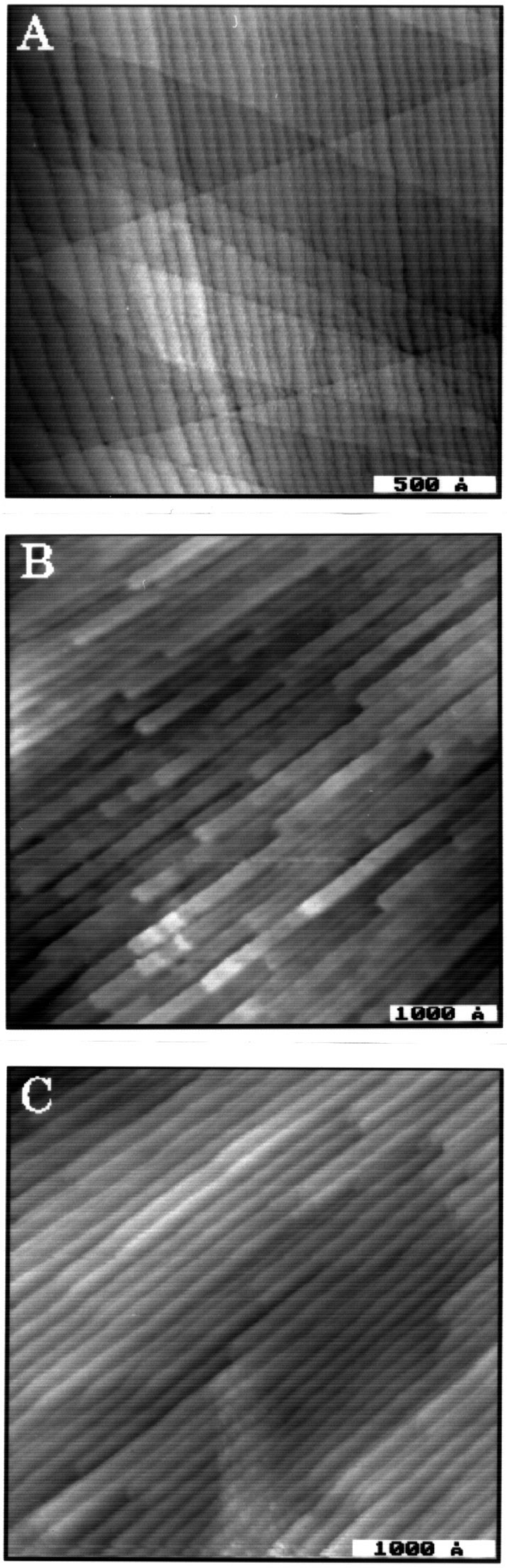

FIG. 4. Topographic mode STM images (A–C) obtained in different parts and at different times of the Pt(111) surface in an atmospheric pressure of a 90% hydrogen/propylene mixture at room temperature. The surface shows terraces (average width 100 Å) and monatomic height steps similar to those seen in the clean Pt(111) surface. In (A), two types of steps are clearly visible. Running more or less vertically are those due to the miscut orientation. These are crisscrossed by much straighter steps forming angles of 60 and 120° with each other. From these, we find that the miscut steps are ∼15° of a close-packed direction. The straight steps are due to emerging dislocations that relieve mechanical stress during annealing. In these pressure and temperature conditions, it is known that the Pt surface is catalyzing the hydrogenation of propylene to propane.

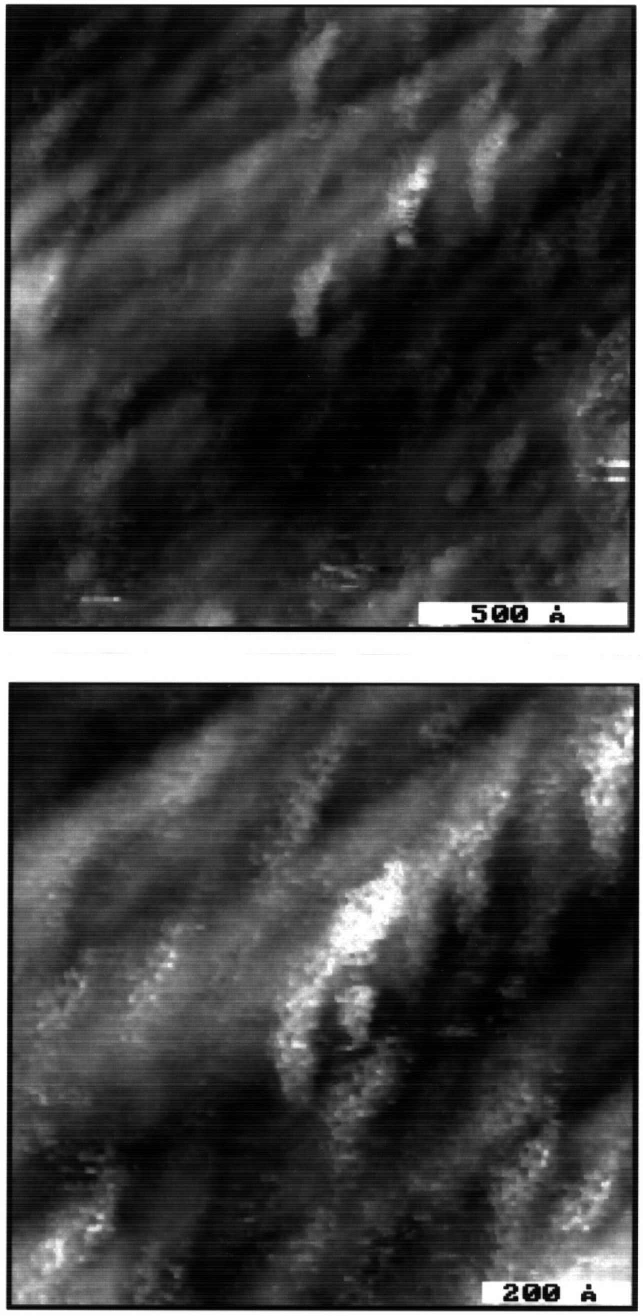

FIG. 5. Topographic mode images at different magnifications, obtained after annealing the surface to 800 K in the atmospheric pressure of 90% hydrogen/propylene. The images show 20–30 Å particles in elongated aggregates (200 Å × 75 Å). The diagonal lines running across the image are monatomic height steps.

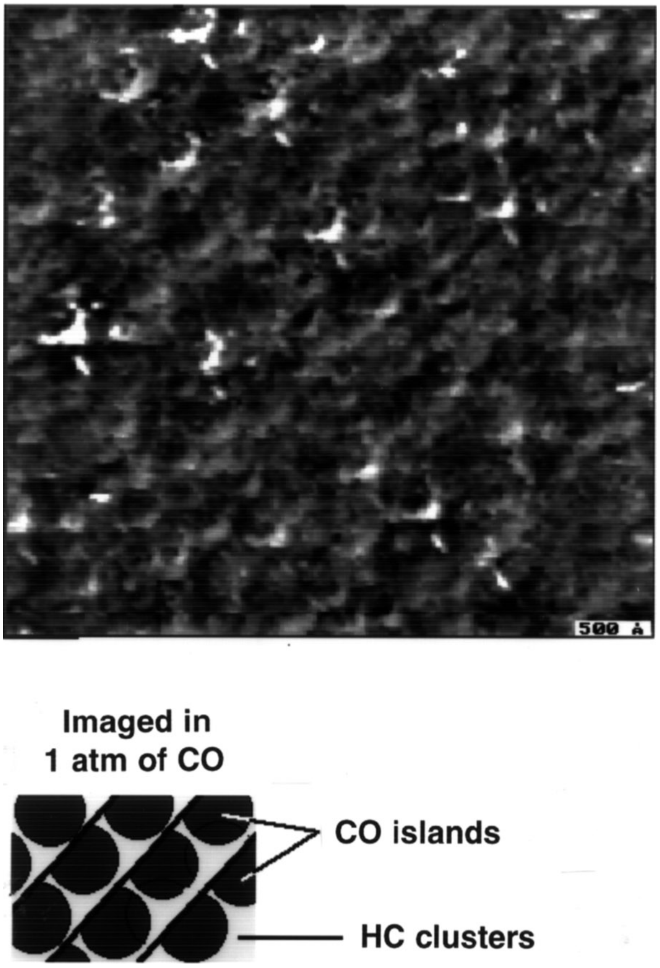

FIG. 6. After annealing to ∼475 K in 0.1 atm of pure CO, carbonaceous clusters were formed which have crescent and overlapping crescent morphologies (some multiple tip effects are present). The clusters have overall dimensions of ∼300 Å and have the same relative orientation relative to the step edges, with the ends of the crescent initiating at the bottom of a step edge and the middle of the crescent extending out to the edge of the terrace. Bottom: Schematic representation of the proposed mechanism for the formation of the crescent-shaped cluster arrangement: CO forms islands starting at the step edges. These islands do not intermix with the carbonaceous clusters and displace them to fill the intervening space.

Annealing the surface to 475 K in this environment resulted in the formation of hydrocarbon clusters which, in the presence of CO, adopt an unusual morphology, as shown in Fig. 6. Carbonaceous clusters arranged in the form of overlapping crescent shape structures with overall dimensions of ∼300 Å (some of the crescent shapes in the image are identical to each other, indicating a multiple tip effect). These structures appear to be influenced by the presence of steps and are oriented with the middle of the crescent extending out to the top of the step edge. This morphology can be explained as due to the presence of segregated islands of carbon monoxide which do not intermix with the carbonaceous species, but rather force them to cluster between the CO islands, as depicted schematically at the bottom of the figure. Removing the CO gas background and replacing it with 1 atm of the original H_2/propylene mixture causes the clusters to redistribute on the surface to form the more isotropic (round) structures, as shown in Fig. 7 and already described in the previous section. The effect of CO pushing aside other chemisorbed species, usually starting from the step edges, has also been observed in the case of S when coadsorbed with CO on Pt (27).

After heating to higher temperatures (500–600 K in CO), the carbonaceous species form roughly circular islands, which have the same diameter as the terrace width (∼150 Å), as shown in Fig. 8. As in the vacuum-annealed samples, the vertical dimension has a bimodal distribution with heights of ∼2.3 and ∼1.2 Å, as shown in Fig. 9. The arrangement of these clusters does not change noticeably after switching the CO environment to H_2/propylene as in the previous case, indicating a much reduced mobility.

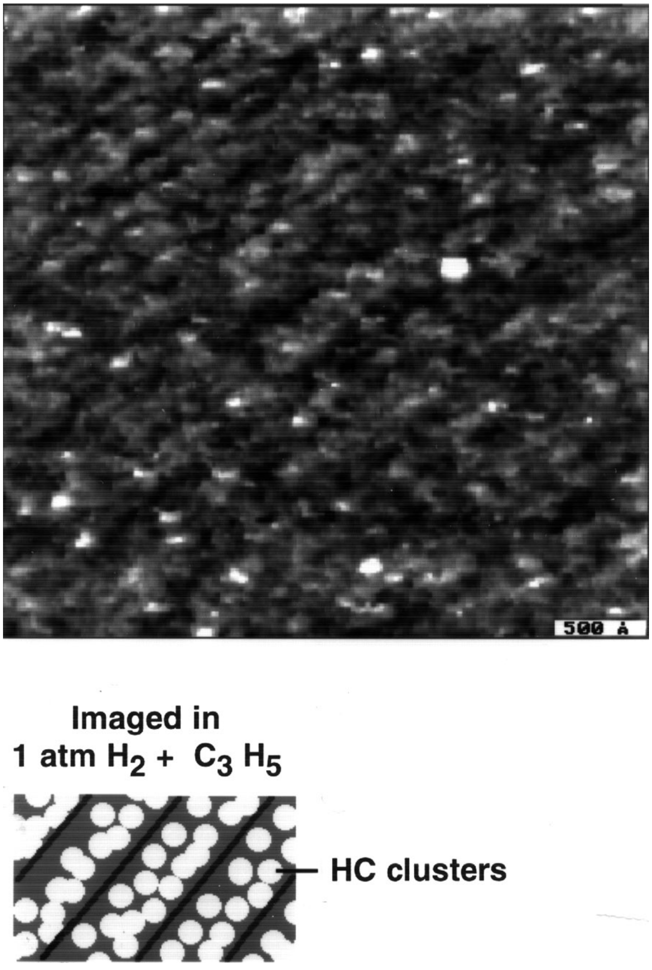

FIG. 7. The morphology of the crescent-shaped clusters reverts back to that of an isotropic distribution when the CO environment was replaced with the 90% hydrogen/propylene mixture. The schematic diagram at the bottom indicates the proposed rearrangement of clusters to a more isotropic distribution.

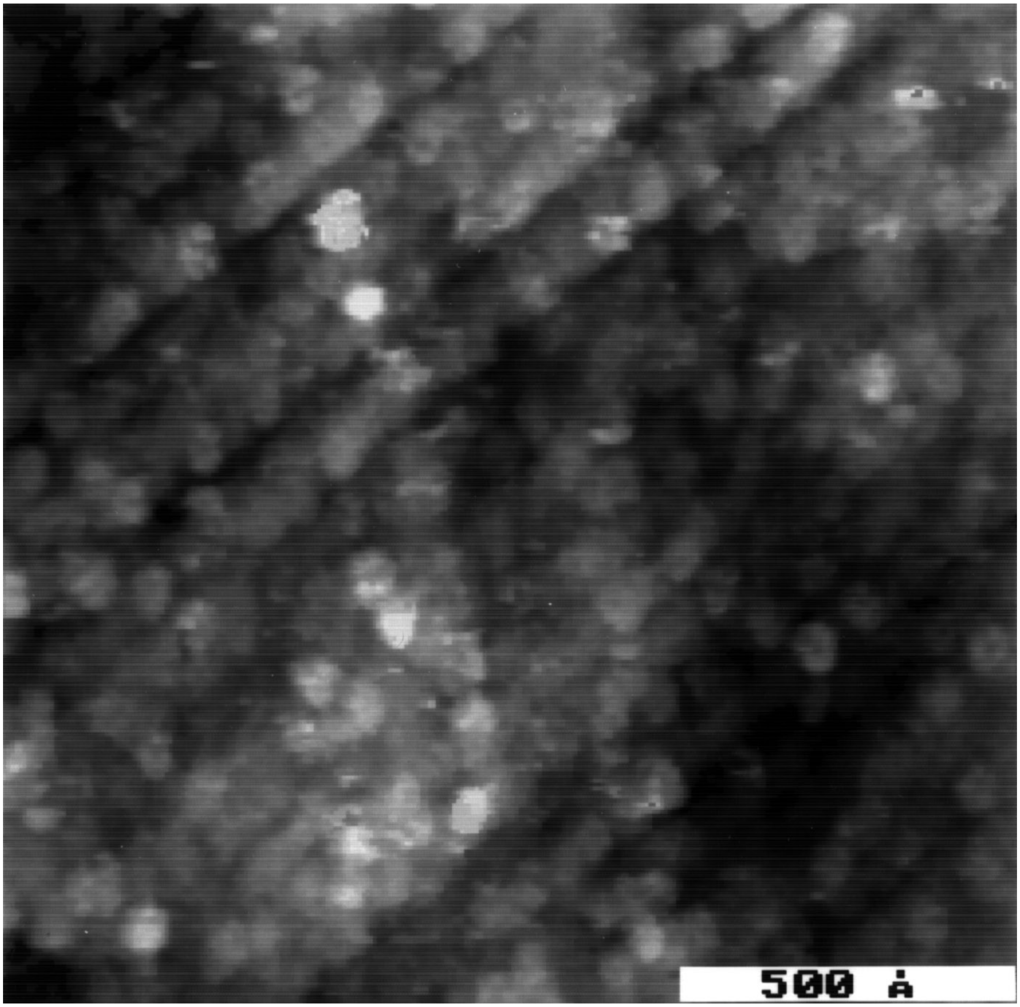

FIG. 8. Annealing to 550 K in CO causes additional loss of hydrogen and the hydrocarbons fragments form circular clusters which have the same diameter as the terrace width (≈150 Å) and a vertical corrugation of one monatomic step height. These clusters can no longer be displaced by coadsorption of CO.

Further dehydrogenation occurs with higher annealing temperatures. The clusters become smaller and more compact, as in the example of Fig. 10. It is interesting to note that, in the presence of CO, no observable change in the step structure occurred when heating to the same temperature that produced step pinning in UHV (800 K), as described in a previous section. This seems to indicate either that the decomposition species are different or that perhaps the presence of coadsorbed CO prevents the attachment of the carbonaceous species to the steps, thus inhibiting their roughening.

DISCUSSION

The experiments described in this paper have produced a number of significant new observations about the surface chemistry of hydrocarbons as they decompose when heated to increasingly higher temperatures under various ambient conditions on Pt(111). First we noticed that the step structure of the platinum surface remains essentially unchanged when covered by the propylidyne monolayer that is formed by the room temperature adsorption of propylene. This is true both in UHV and under catalytic reaction conditions of atmospheric pressures of H_2/propylene mixtures. The stability of the step structure is maintained even when moderate decomposition leaving small fragments takes place (after heating to ~550 K in UHV). Severe dehydrogenation, however, results in graphite formation and causes step pinning, a phenomenon observed previously by Land *et al.* using ethylene, although in that case the temperature used was 1200 K.

An interesting observation is that, in the presence of other adsorbates (CO and H_2/propylene mixtures) under atmospheric pressure conditions, step pinning does not

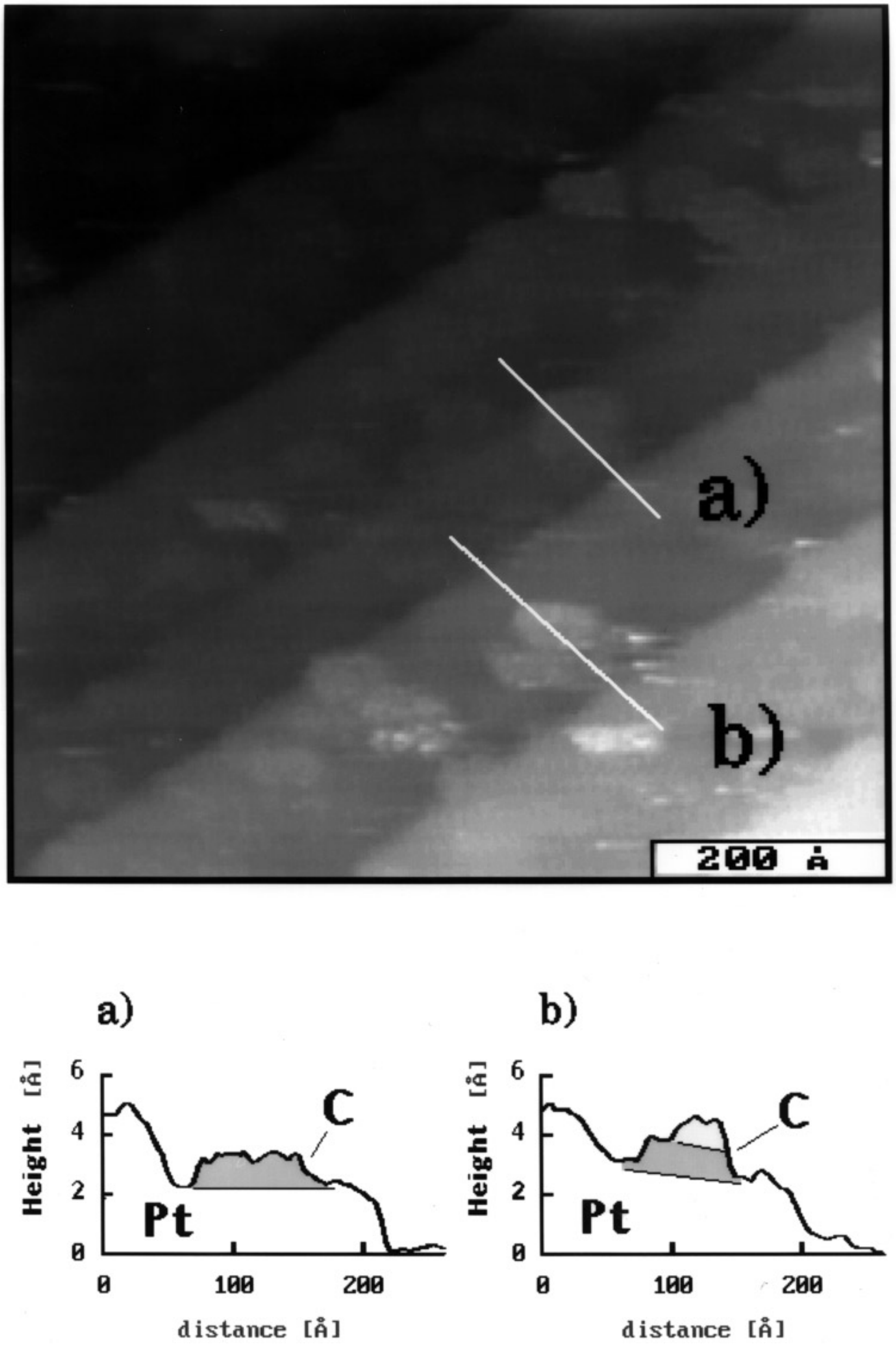

FIG. 9. 740 × 740 Å image obtained after annealing to ∼550 K in 0.1 atm of CO. The carbonaceous clusters are seen in many different locations: near the top and bottom of step edges, and in the center of the terraces. Their heights are found to be close to one Pt step height (∼2.3 Å) or half that value. Clusters with low and high parts are also present, as illustrated in the examples of the two profiles (a), (b) at the bottom.

occur, even at temperatures of 800 K and above. In the case of H_2-rich environments, rapid rehydrogenation of unsaturated fragments occurs which might prevent the formation of strong Pt–C bonds. CO, on the other hand, might block step sites, thus preventing pinning by the carbon particles. Thus, in the presence of coabsorbates, the steps remain, on the average, straight and in the direction determined by the miscut orientation of the crystal. An exception are the steps generated by dislocation motion during thermal annealing that produce new surface steps. These are easily recognized

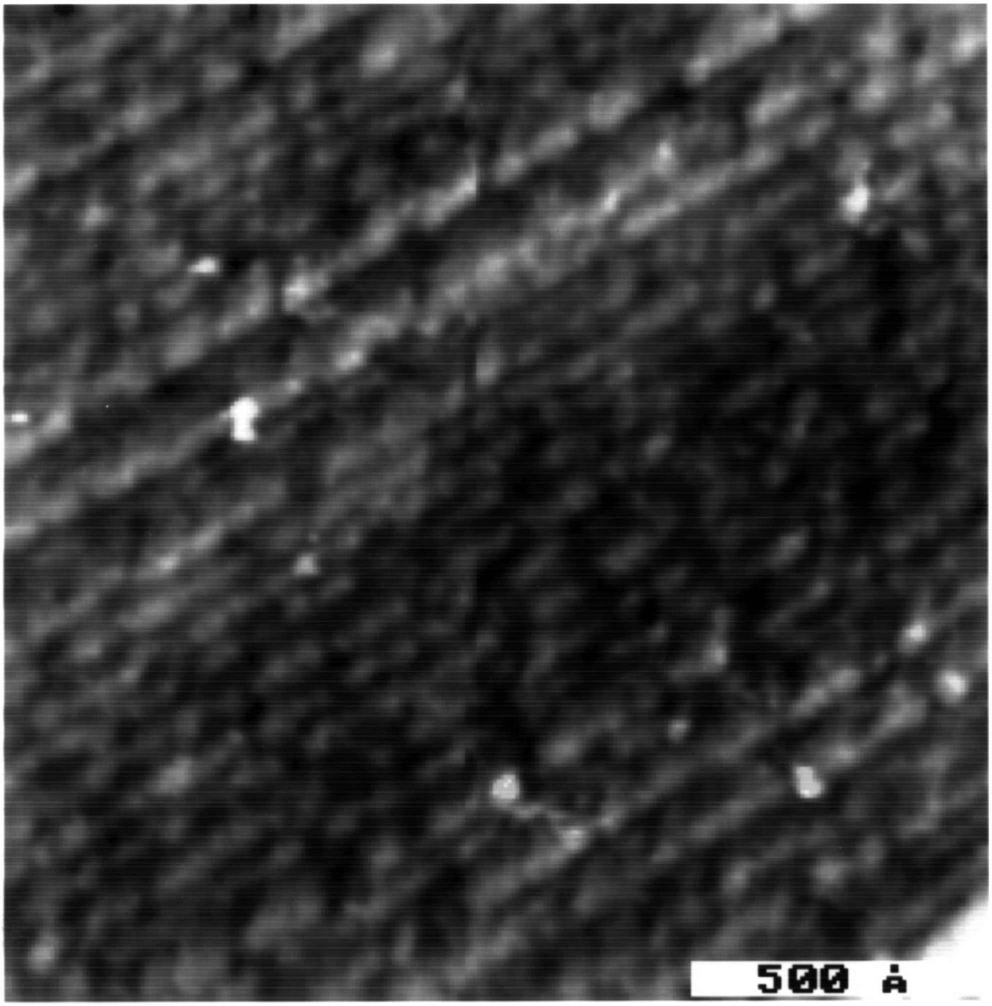

FIG. 10. Annealing to higher temperatures (700 K) results in the further loss of hydrogen and the clusters become smaller and more compact. In tip-mediated catalysis experiments [28, 29], these clusters could no longer be reacted away.

by their geometry as they crisscross the misorientation steps and each other at angles in accordance with the fcc crystal structure of platinum (see Fig. 4A).

The hydrogen species evolve during annealing due to increased loss of hydrogen and polymerization of the resulting fragments. In the presence of 0.1 atm of CO, dehydrogenation appears to proceed at temperatures that are not too far from those found in UHV. In both cases, heating to ∼450 K decomposes the propylidyne species, as seen by thermal programmed desorption of H_2 in UHV and by the formation of clusters in CO environments in the present STM experiments. In UHV, however, the clusters remain smaller and are not visible in the STM images until ∼550–600 K. It is possible that the compression of the fragments by the coadsorbed CO makes polymerization more efficient due to their higher surface density.

Another interesting observation refers to the mobility of the hydrocarbon clusters. As we have seen, the degree of decomposition in CO at 475 K is such that the clusters move easily on the surface as they are compressed by CO. After heating at 600 K, however, the clusters can not be moved or "pushed" by the coadsorbed CO. This indicates that the additional loss of hydrogen occurring at the higher temperature creates more C bonds to the Pt substrate, thus reducing their mobility. These observations are in line with our recent findings of the catalytic rehydrogenation of the clusters by the STM Pt tip in H_2 and O_2 environments (28, 29). In these tip-catalysis experiments, efficient rehydrogenation (or oxidation) occurred only on clusters prepared by heating up to 600 K and could not be observed when the clusters were prepared by heating to 800 K and above. This indicates that severe dehydrogenation and formation of more Pt–C bonds lowers both the efficiency of rehydrogenation (or oxidation) rate by the tip and the cluster mobility.

Finally, it is important to stress that STM studies could be carried out on the Pt(111) surface while in atmospheric pressures of H_2/propylene mixtures. This is the first time STM experiments have been carried out on a surface while exposed to an atmospheric pressure of reactant gases in which the sample is catalytically active. In this environment at 300 K, the catalyst surface was stable on a mesoscopic scale, i.e., there was no large scale restructuring of the surface or formation of carbonaceous clusters characteristic of hydrocarbon decomposition.

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