Scanning Tunneling Microscopy Investigation of the Conversion of Ethylene to Carbon Clusters and Graphite on Pt(111)

Viktor Joha#nek, Ana B. De La Ree, and John C. Hemminger

J. Phys. Chem. C, 2009, 113 (11), 4441-4444 • DOI: 10.1021/jp810298w • Publication Date (Web): 24 February 2009

Downloaded from http://pubs.acs.org on March 31, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
Scanning Tunneling Microscopy Investigation of the Conversion of Ethylene to Carbon Clusters and Graphite on Pt(111)

Viktor Johánek,† Ana B. De La Ree, and John C. Hemminger*  
Department of Chemistry and Institute for Surface and Interface Science, University of California, Irvine, 1102 Natural Science II, Irvine, California, 92697-2025  

Received: November 23, 2008; Revised Manuscript Received: January 18, 2009

The dehydrogenation of ethylene on Pt(111) was studied by scanning tunneling microscopy (STM) under ultra-high vacuum conditions. Previous experiments have shown that thermal dehydrogenation following saturation exposure of ethylene on Pt(111) resulted in the formation of well-defined carbon clusters. The aggregation to form the carbon clusters leaves open Pt areas that could be available for additional adsorption. It had not been previously determined whether the adsorption and dehydrogenation of additional ethylene would lead to the growth of the initial clusters or the nucleation of additional clusters of the same size. The present study confirms previous reports that the initial carbon clusters are 15 ± 2 Å in diameter, 2.5 ± 0.3 Å in height, and contain an average of 34 ± 9 carbon atoms per cluster. We show that exposing this surface to additional ethylene at room temperature and annealing leads to an increase in the number of particles of the same size, with no growth in size of the initial particles. Dosing and dehydrogenation/annealing cycles were repeated until the dehydrogenation activity of the Pt(111) surface was completely suppressed, which occurred after the fourth such cycle. Continued cycling leads to the beginning of the formation of a graphite adlayer on the platinum, presumably via agglomeration of the clusters at a high cluster density.

Introduction

The formation of a variety of forms of carbon on platinum has been widely studied as a model system for heterogeneous catalysis.1–7 This arises mainly from the indication that some forms of carbon may have substantial influence on surface reactivity. Original reports suggest that all carbon quenched catalytic activity of transition metals,1,3 However, recent studies indicate distinct catalytic activity as a result of the well-defined structural differences from various carbon sources. For instance, a graphitic layer causes a poisoning of the platinum surface toward dehydrogenation of alkenes, while less atomically ordered carbonaceous particles demonstrate an attenuated degree of poisoning.1,8

Given the relationship between catalytic activity and the poisoning level caused by different structural carbon moieties, a detailed understanding of the transitions of these carbon particles on catalytic surfaces is of great interest. The structural differences between various forms of carbon are related to the generation mechanism, as well as to the initial source of carbon.1 In studies that utilize single-crystal model catalyst surfaces, in general two methods of carbon formation have been generally studied. One method is by adsorbing a hydrocarbon at or below room temperature followed by annealing to completely dehydrogenate the molecule. A second method exposes the hydrocarbon to a sample which is resting at an elevated temperature.4 The dehydrogenation of aromatics, such as naphthalene, on Pt(111) leads to unstructured patches of carbon.9–11 On the other hand, dehydrogenation of ethylene on Pt(111) converts in a distinct manner into individual carbon particles and eventually graphite by way of a uniform intermediate species, ethylidyne.12,13

Land et al. demonstrated that an initial step in the thermal dehydrogenation of the ethylidyne surface species on Pt(111) resulted in the formation of well-defined carbon clusters.13

The formation of these carbon clusters by aggregation of the partially dehydrogenated ethylidyne leaves open Pt areas available for additional adsorption. However, it had not been previously determined whether the adsorption and dehydrogenation of additional ethylene would lead to growth of the initial clusters or to nucleation of additional clusters of the same size. We have utilized ultra-high vacuum (UHV)—variable-temperature scanning tunneling microscopy (VT-STM) to address this question.

Here we report repeated dosing of ethylene onto the surface at room temperature followed by annealing, which leads to an increase in the number of carbon clusters without an increase in the size of previously produced clusters. The Pt(111) dehydrogenation activity was completely suppressed after four such cycles. The only growth in cluster size that was observed was due to agglomeration of clusters once the surface was covered with a high density of clusters. Continued cycles lead to the formation of a graphite adlayer on the platinum (presumably via agglomeration of the clusters at high cluster density). This was observed at temperatures well below the onset of long-range graphene formation in the single ethylene dose experiments.

Experimental Section

Imaging experiments were performed using a UHV—variable-temperature scanning tunneling microscope (UHV 300 VT-STM, RHK Technology, Inc., Troy, MI) that was installed on a custom chamber with a base pressure less than 1 × 10−10 Torr. The scanning tunneling microscope is coupled to a secondary UHV chamber with standard techniques for sample preparation and characterization such as low-energy electron diffraction (LEED, PHI model 15–120) and Auger electron
spectroscopy (AES, PHI model 10−155, single-pass CMA), which will be described in detail elsewhere.14 A 99.999% purity Pt(111) single crystal (MaTecK, Jülich, Germany) of ~9 mm diameter and 1.5 mm thickness with an average (111) terrace width of 200 nm, was heated radiatively by passing current through a Re filament mounted ∼2 mm below the sample. The Pt single crystal was cleaned by bombardment of the sample with Ar\(^+\) ions (\(I_{\text{Ar}^+} = 0.90 \mu\text{A} \) at 600 eV, \(T_{\text{sample}} = 838 \text{ K}, \) for 35 min). The ion bombardment was followed by oxygen treatment at 700 K (partial pressure of \(1.8 \times 10^{-6} \text{ Torr}, \) 30 min). The sample was then flash annealed to 850 K in vacuum. This procedure was repeated until a clean, well-annealed sample was produced. The surface processed in this manner exhibits large (111) terraces and is free of carbon and other contaminants as characterized by AES. The sample was then transferred under UHV into the STM chamber for imaging and exposure to ethylene (research grade, 99.999%, Matheson Tri-Gas, Newark, CA). The sample was exposed to 20 langmuir (1 langmuir = \(10^{-6} \text{ torr s}\)) of ethylene through back-filling of the chamber, after which it was annealed to 700 K (partial pressure of \(1.8 \times 10^{-6} \text{ Torr}, \) 30 min). The sample was then flash annealed to 850 K in vacuum. This procedure was repeated until a clean, well-annealed sample was produced. The surface processed in this manner exhibits large (111) terraces and is free of carbon and other contaminants as characterized by AES. The sample was then transferred under UHV into the STM chamber for imaging and exposure to ethylene (research grade, 99.999%, Matheson Tri-Gas, Newark, CA). The sample was exposed to 20 langmuir (1 langmuir = \(10^{-6} \text{ torr s}\)) of ethylene through back-filling of the chamber, after which it was annealed to 700 K, thus completing one cycle. Previous studies have demonstrated that 700 K corresponds to the temperature at which dehydrogenation of adsorbed ethylene and the resultant hydrocarbon fragments is just complete, thus leaving the surface free of all hydrogen.15,16 These exposure/annealing cycles were repeated up to six times while imaging in between the various steps. All STM images were obtained in the constant current mode with tunneling currents of 1.0 ± 0.5 nA and typical bias voltages of 50 mV applied to the tip. The \(z\)-dimension of the STM images was calibrated using the known 2.3 Å step height of the Pt(111) surface.17

Results and Discussion

The elementary steps of ethylene dehydrogenation on Pt(111) under UHV conditions have been described elsewhere.7,12,13,15 The goal of this work was to examine how a Pt(111) single crystal covered with carbon clusters would react to additional ethylene dosings. All the ethylene exposures were done at room temperature in order to reduce the experimental time frame, and hence minimize the undesired coadsorption from the chamber residual gas-phase species. At this temperature, ethylene converts directly to ethylidyne, forming the adsorbate with the same surface density as in the case of low-temperature (160 K) ethylene exposure followed by annealing to 300 K, which was verified by independent STM experiments. At room temperature, however, slightly larger doses of ethylene are required to obtain saturation coverage (20 langmuir at 300 K compared to 2.5 langmuir at 160 K) due to the competing ethylene desorption reaction.

Although ethylidyne was not directly visible in the STM images due to its high surface mobility at room temperature,13,18,19 the carbonaceous particles formed after 700 K annealing (and complete hydrogen removal from the surface) are easily resolved. The series of images presented in Figure 1 show the evolution of surface structure with increasing number of ethylene exposure/annealing cycles. After the first cycle, randomly distributed carbonaceous particles are formed on the Pt surface. No preferential occupation of steps or other surface sites with different coordination (such as defects) has been observed in accordance with other reports.4,13,15

The surface density of particles, as well as their size, has been determined by STM image analysis. After the first experimental dosing and heating cycle, the majority of particles (around 95%) appear as flat and circular single atomic layer islands having a relatively uniform size distribution with an average diameter in the plane of the Pt surface of \(20 \pm 2\) Å and an average height of \(2.2 \pm 0.3\) Å. By measuring a monatomic step on the clean Pt surface, we can approximate the convolution associated with the STM tip shape. From this we can estimate their real size to be \(\sim 15 \pm 2\) Å. This would correspond to an average number of \(34 \pm 9\) carbon atoms per particle. These results are identical to what we have previously seen after ethylene dosing at 160 K on the same system with STM.13,15

Furthermore, this quantitative analysis can be cross-checked with a calculation based on the measured surface density of carbon islands with respect to the density of Pt(111) surface.

---

**Figure 1.** STM images (200 × 115 nm\(^2\)) obtained at 298 K on (a) clean Pt(111) sample and after each (b–g) ethylene adsorption/annealing cycle. In each cycle, the sample was exposed to 20 langmuir of C\(_2\)H\(_4\) at 298 K and subsequently flash-annealed at 700 K.
atoms \((1.51 \times 10^{15} \text{ cm}^{-2})\) and the known saturation coverage for ethylene chemisorption on Pt(111), which is \(0.21 \pm 0.02\), assuming that all adsorbed ethylene converts completely into carbon and that carbon does not dissolve into the bulk. After the first ethylene/Pt annealing the density of particles was \(9.9(\pm 0.7) \times 10^{12} \text{ cm}^{-2}\). Thus, each carbonaceous particle consists of an average of \(32 \pm 5\) carbon atoms, in good agreement with the number calculated from particle size analysis.

When the initial adsorption/annealing procedure is followed by the second cycle, additional particles are generated on the surface, again with a random spatial distribution. This provides evidence that the dehydrogenation activity is not completely suppressed after one adsorption and annealing cycle. The image analysis yields the same size distribution as after the first cycle, indicating that the existing particles do not grow in size, but rather new particles are produced in the empty space remaining following the previous ethylene dehydrogenation. It is interesting that the carbon particles do not grow in size, but rather remain at this stable size of about 34 carbon atoms. Further studies are currently being performed to determine a reason for this phenomenon. The same trend continues with successive adsorption/annealing cycles resulting in almost complete inhibition of Pt catalytic activity toward ethylene dehydrogenation after four cycles. In Figure 2, the evolution of the average carbonaceous particle density with the number of adsorption/annealing cycles is presented. For each cycle Figure 2 also shows the relative overall surface dehydrogenation activity, which was calculated as a ratio of the amount of carbon generated during the annealing to the area of the open Pt surface available prior to the ethylene dosing of the particular cycle. Notably, the activity goes to zero after four cycles even though there is still about 70% of Pt surface physically not covered with carbon. This suggests that there is either (a) a minimal space required for ethylene to undergo the whole dehydrogenation process to finally form carbon or (b) the catalytic and/or adsorption properties of partially carbon-covered platinum is altered in the vicinity of carbon deposit compared to pristine Pt(111). The average distance between the particles after sixth cycle is 3.4 nm, which corresponds to the spacing between particles edges of 1.9 nm (taking into account particle average size of 1.5 nm) and can give us a rough idea about the spatial scale of these effects.

The first possibility (a) suggests that a clustering of ethylene or its dehydrogenation intermediates (i.e., an ensemble effect) is necessary to facilitate the dehydrogenation/agglomeration process and thus favor it against the competing thermal desorption reaction. This is supported by the observation of spatial separation between the ethylene and ethylidyne phases during the conversion from one to another, as we have shown previously. Without clustering, the latter could only be explained if the surface species were sufficiently mobile on the platinum surface under our experimental conditions. This is possible for ethylidyne, which has a low activation energy for surface diffusion on Pt(111) of 0.109 eV. In this case, however, there would also have to exist a driving force for the fragments to diffuse preferentially toward the nucleation centers that had already been formed or the local reactivity around the particles would have to be enhanced. Such behavior is not observed, as adding more ethylene after first cycle does not lead to an increase in particle size. However, the second mechanism (b) cannot be fully excluded.

The vast majority of the carbonaceous particles on the sample surface do not grow in size with increasing number of ethylene exposures and annealings. However, there is a small fraction of particles that exhibit further growth. The occurrence of laterally enlarged particles is due to the spatial packing causing coalescence rather then the surface diffusion because the carbonaceous particles are known to be immobile on the Pt(111) surface. In Figure 3, STM line scans after first and sixth cycle are shown. The cross-section taken after six cycles reveals particles with multiple atomic layers. After the final annealing, the relative quantity of double-layered particles amounted to 16% and particles with three or more layers of carbon to about 2% of the total number. This can be compared to less than 5% of double-layered particles found after the first annealing of ethylene.

Following the sixth annealing cycle, it was also found that on some portions of the sample a continuous graphite layer had formed (with the characteristic Moiré pattern resulting from higher-order commensurability of hexagonal (0001) lattice of graphite and the Pt(111) lattice as has been reported elsewhere), as shown in Figure 4. These graphene sheets evolved mainly at the lower step edges of the (111) terraces. In previous experiments that involved only one adsorption/annealing cycle, the transition from non-graphitic to graphitic phase was observed after only significantly higher annealing temperatures exceeding 800 K and large continuous structures of graphite were observed to form only at temperatures above 1000 K. This could be explained by lowering the activation barrier for carbon phase transitions...
Just a small fraction of particles grow as they coalesce and/or form a second atomic layer of carbon. As the carbon saturation coverage was surpassed, the formation of a graphite adlayer on the platinum was observed. This was achieved presumably via agglomeration of the clusters at high cluster density. This was observed at temperatures well below the onset of long-range graphene formation in a single ethylene dose experiment.

Acknowledgment. This research has been supported by the U.S. Department of Energy (Grant No. DE-FG02-96ER45576) and the NASA-Jenkins Predoctoral Fellowship Program.

References and Notes