Electronic Supplementary Information

Mobility on the Reconstructed Pt(100)-hex Surface under Ethylene and its Mixture with Hydrogen and Carbon Monoxide

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1. Clean Pt(100)-hex without waves

Figure S1 shows the structures of a clean Pt(100)-hex surface in UHV while scanning perpendicular to the stripes. The stripes appear straight rather than distorted, which indicates that the presence of C_2H_4 -related adsorbates on Pt(100)-hex is crucial for inducing the distortions in Figure 1. The displacement of the hexagonal first layer is due to the weakened interactions between the surface and the bulk layers, as a result of ethylene adsorption.



Figure S1. STM images of the clean Pt(100)-hex surface when scanning perpendicular to the stripes. The tip scans (a) from top to bottom and (b) from bottom to top. No surface waves as in Figure 2 are observed.

2. Line profiles in STM images

Figure S2 shows the STM image of Pt(100) under 500 mTorr of C_2H_4 and 500 mTorr of H_2 , which was acquired at the scan rate of 150 nm/s. The stripes, although breaking into short pieces, indicate that the hexagonal reconstruction is roughly maintained. The topography profile of the blue line vertical to the stripes shows that the average periodicity between the stripes remains at ~1.4 nm. Some bright spots with ~600 pm in diameter and ~50 pm in height appear on the stripes, as shown by the topography of the black line.

Adding 3 mTorr of CO into the C₂H₄-H₂ mixture leads to the complete lifting of the hexagonal reconstruction on Pt(100). A large amount of Pt islands form across the surface by the excess Pt atoms in the initial hexagonal surface layer. The line profile in Figure S3 shows that the islands are ~2 nm in size and ~120 pm in height. An important question under such condition is whether CO, C₂H₄ and H₂ are mixed or not during co-adsorption. If these molecules are segregated on Pt(100), domains with islands induced by CO and stripes stabilized by C₂H₄ should be both observed under STM. As the island structure is observed all across the surface with no stripes, CO, C₂H₄ and H₂ are likely to co-adsorb in a mixed phase.



Figure S2. (Left) STM image of Pt(100) under 500 mTorr of C₂H₄ and 500 mTorr of

 H_2 at 150 nm/s. (Right) line profiles (blue) vertical to the stripes and (black) along the stripes.



Figure S3. STM image of Pt(100) acquired at 60 nm/s after adding 3 mTorr of CO into the C_2H_4 - H_2 mixture, and the line profile along the islands.

3. XPS analysis

The ambient-pressure X-ray photoelectron spectroscopy experiments were performed at Advanced Light Source in Lawrence Berkeley National Laboratory.^{1, 2} The Pt(100)-hex crystal is cleaned by repeating cycles of Ar^+ sputtering, annealing under O₂ at 923 K and annealing in vacuum at 1073 K until no impurity is seen in the XPS survey spectrum. Pt 4f, C 1s and O 1s core level spectra were collected with incident X-ray photon energies of 340, 570 and 810 eV, respectively. The kinetic energies of the photoelectrons were thus kept at ~280 eV for all the three elements, which ensures the same probing depth at ~0.6 nm. All the XPS spectra were calibrated with respect to the Fermi edge that was set to 0 eV.

After subtracting the Shirley-type background to each Pt 4f and O 1s spectrum,³ the areas of Pt 4f and O 1s are calculated. The CO coverage is estimated based on the O 1s to Pt 4f peak area ratio, with a calibration using 0.50 monolayer (ML) CO on Pt(557) at 5×10^{-9} Torr.⁴ The coverage of C₂H₄ is estimated through the C 1s to Pt 4f area ratio, by assuming the same sensitivity of carbon atoms in ethylene and CO. Under 900 mTorr of C₂H₄, a total amount of ~0.83 ML C₂H₄ is present at the Pt(100)

surface. After decreasing the C_2H_4 pressure to 500 mTorr and introducing 10 mTorr of CO, the C_2H_4 coverage decreases to ~0.78 ML and ~0.30 ML CO chemisorbs onto the Pt(100) surface. The amount of adsorbed CO is more than that of desorbed C_2H_4 , since CO compresses the existing C_2H_4 , and because the CO-induced island formation opens more adsorption sites on the surface. Accordingly, the Pt(100) surface can accommodate more adsorbates in the co-adsorption of C_2H_4 and CO.



Figure S4. (Left) C 1s and (right) O 1s core level spectra of Pt(100) under (a) UHV, (b) 900 mTorr of C_2H_4 , and (c) 500 mTorr of C_2H_4 and 10 mTorr of CO. The estimated C_2H_4 and CO coverage is also shown.

Carbon contamination, which usually appears as hydrocarbons at ~284 eV in AP-XPS, may cause a problem in estimating the ethylene coverage. Before performing the AP-XPS experiments, the vacuum chambers were baked under O_2 at 120 °C for a day so as to best remove the hydrocarbon contaminants. Limited by the instrument access, a C 1s spectrum was acquired under 5 mTorr of CO on Pt(332) in another experiment as the reference and the spectrum is shown in Figure S5. The area of hydrocarbon peak at 284 eV is ~5% of the area of CO peak at ~286 eV. If we roughly assume the same area ratio of hydrocarbon to CO peak, the amount of hydrocarbon in Figure S4 is equivalent to only 0.02 ML ethylene. Therefore over 90% of the ethylene-related adsorbates (0.76 ML out of 0.83 ML) remain on the Pt(100) surface after dosing CO.



Figure S5. C 1s spectrum of Pt(332) under 5 mTorr of CO.

In addition to the changes in coverage, the position of C 1s peaks have also shifted after introducing CO. Two peaks can be observed at 900 mTorr of C_2H_4 . The peak at 286.9 eV corresponds to gas-phase C_2H_4 and the other at 284.2 eV corresponding to the C_2H_4 -related adsorbates, mainly ethylidyne and di- σ -bonded ethylene.⁵ With the introduction of CO, the adsorbed C_2H_4 peak shifts down towards 284.0 eV. This peak shift suggests that the chemical state of the C_2H_4 adsorbate has changed, most likely into vinylidene. The C 1s peak of chemisorbed CO is buried under the gas-phase C_2H_4 peak that shifts to 286.5 eV, as CO adsorption changes the sample work function.

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