Hydrogenation of Phenylacetylene to Styrene on Pre-C$_x$H$_y$- and C-Covered Cu(111) Single Crystal Catalysts

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Thermal hydrogenation of phenylacetylene (PA, C$_8$H$_8$) to styrene (C$_8$H$_8$) on pre-C$_x$H$_y$- and C-covered Cu(111) single crystal substrates has been studied using temperature-programmed desorption (TPD) mass spectrometry. Chemisorbed PA with an acetylene group has been proved to be associated with hydrogen of pre-adsorbed C$_x$H$_y$ to form styrene (104 amu) on Cu surface. For the parent (PA) mass (102 amu) TPD profile, the TPD peaks at 360 K and 410 K are assigned to chemisorbed vertically aligned PA and flat-lying cross-bridged PA, respectively (J. Phys. Chem. C 2007, 111, 5101). The relative I$_{360K}$/I$_{410K}$ TPD ratio dramatically increases with increasing pre-adsorbed C$_x$H$_y$ before dosing PA, while the ratio does not increase for pre-C-covered surface. For PA on pre-C$_x$H$_y$-covered Cu(111) surface, styrene desorption is enhanced relative to the parent PA desorption, while styrene formation is dramatically quenched on pre-C-covered (lack of adsorbed hydrogen nearby) surface. It appears that only cross-bridged PA associates with adsorbed hydrogen to form styrene that promptly desorbs at 410 K, while vertically aligned PA is less likely to participate in forming styrene.

Key Words: Hydrogenation, Temperature-programmed desorption, Phenylacetylene, Styrene

Introduction

Hydrogenation reaction of unsaturated compounds and dehydrogenated reactant intermediates are one of very important key steps in producing desired products from natural resources, and for understanding many corresponding catalysis reactions.1-4 The hydrogenation reactions occur either in high-pressure hydrogen atmospheres5 or on catalytic metal (or semiconductor) surfaces.6-8 On metal surfaces, adsorbed hydrogen atoms could associate with other adsorbed species (e.g., hydrocarbon intermediates) to form various hydrogenated or saturated hydrocarbon products.1 For example, an adsorbed CH$_2$ and an atomic H associate to form CH$_3$.7 The reactivity of hydrogenation reaction depends on many factors such as catalytic activity of a substrate and geometry of an adsorbate.10,11 For adsorbed ethylene and benzene on Cu(111), the adsorbed molecules more plausibly react with atomic hydrogen in gas phase than with adsorbed atomic hydrogen.12 Selective hydrogenation reaction is also of very importance. Pd catalysts have been used for the removal of acetylene impurity from ethylene without forming ethane from ethylene.13 Additionally, the selective hydrogenation of PA to styrene is of importance to obtain pure styrene without producing other products such as ethylbenzene.14,15

In this paper, we study hydrogenation reaction of PA on Cu(111) single crystal surface pre-covered with two different (C$_x$H$_y$- and C-covered) adsorbates using temperature-programmed desorption (TPD). Phenylacetylene (PA, C$_8$H$_8$, 102 amu) contains an acetylene group and an aromatic benzene ring, and this molecule is one of the best model systems for studying hydrogenation reaction.

Experimental Section

Temperature-programmed desorption (TPD) spectroscopy was performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of less than 5 × 10$^{-10}$ Torr. A time-of-flight mass spectrometer (TOF-MS) was used for collecting TPD spectra at a temperature ramp rate of 2 K/sec. The Cu(111) single crystal (13 mm diameter × 2.5 mm thickness, MaTeCK) surface was cleaned by cyclic Ar+ ion sputtering and annealing, and the cleanliness was checked by either Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS). The substrate could be heated by resistive heating of a tungsten wire and cooled to 100 K by contacting with a liquid nitrogen cooling holder. The temperature was measured with a chromel-alumel thermocouple wire connected on the edge of the substrate.

Phenylacetylene (Acros, 99.8%, molecular weight = 102 amu) was dosed on Cu(111) at 100 K through a leak valve connected to a stainless steel tube (3 mm of inner diameter). The distance from the edge of the tube to the Cu(111) surface was about 4 cm. The pressure behind the leak valve was at 0.5 torr, and the amount of dosage was controlled by exposure time (sec). The phenylacetylene (PA, C$_8$H$_8$) was fully degassed by repeated freeze-pump-thaw cycles before dosing.

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A pre-hydrocarbon (C₆H₄) covered Cu(111) surface was achieved by dosing multilayer (2-3 monolayers, ML) PA on clean Cu(111) at 100 K and then annealing to 520 K. A thicker C₆H₄-covered Cu(111) was achieved by cooling the pre-C₆H₄-covered Cu(111) surface to 100 K, redosing multilayer PA and then reannealing to 520 K. A pre-amorphous carbon (C)-covered (lack of hydrogen) Cu(111) surface was realized as follows. The multilayer PA on clean Cu(111) at 100 K and then annealing to 520 K. A pre-amorphous C₆H₄-covered Cu(111) was achieved by cooling the pre-C₆H₄-covered Cu(111) surface to 100 K, redosing multilayer PA and then reannealing to 810 K, and recooled to 100 K. And then, multilayer PA was redosed on the substrate, and reannealed to 810 K.

Results and Discussion

To facilitate understanding of our present study on hydrogenation of PA on pre-adsorbate-covered Cu(111) surface, we first briefly describe our previous works on thermal desorptions and reactions of PA on clean Cu(111). In the TOF-MS TPD spectra of PA on clean Cu(111) dosed at 100 K, major desorption peaks include H₂ (2 amu), C₂H₂ (26 amu), C₆H₆ (102 amu), C₆H₅ (104 amu) and C₆H₁₀ (106 and 91 amu). Broad reaction-limited H₂ (2 amu) desorption peaks starts from 230 K and ending at around 780 K. The plausible reaction processes include 2H (ad, adsorbed) → H₂(g), 2C₆H₆(ad) → 2C₆H₅(ad) + H₂(g), and H(ad) + C₆H₆(ad) → C₆H₅(ad) + H₂(g). The acetylene (C₂H₂, 26 amu) desorption peak at around 350 K is likely a reaction limited process e.g., H(ad) + HCC(ad) → C₆H₅(g) and/or H(ad) + H(ad) = C(ad)C₆H₆(ad) → C₆H₅(g) + C₆H(ad). The very weak peaks of 106 and 91 amu at 250 K (not shown here) are assigned to ethylbenzene (C₆H₁₀) contained in the PA sample as an impurity.

With an emphasis of a hydrogenation product of PA, Figure 1 shows the TPD profiles (102 and 104 amu) of a set of experiments designed to compare PA on clean Cu(111) with PA on pre-adsorbate-covered Cu(111). Figure 2 plots the TPD peak areas of 102 and 104 amu of Figure 1(a), 1(b) and 1(c). Two different adsorbate-covered Cu(111) surfaces are pre-C₆H₄- and C-covered, described in Experimental Section. The major difference is that pre-C₆H₄-covered surface provides PA with hydrogen for hydrogenation reaction while the pre-C-covered surface does not. Upon annealing of PA on clean Cu(111) to 520 K, the Cu(111) surface could be pre-covered by dissociated PA, presumably C₆H₅ form. C₆H₅ (x ≤ 6 and y ≤ 5) is assumed to be acyclic hydrocarbons and fragments formed from phenyl (C₆H₅). The simplest form is assumed to be =C(ad)-H. On the basis of 2 amu TPD (will be shown in Figure 3), the only C-covered surface could be achieved by annealing to 810 K because hydrogen is almost completely desorbed after 810 K annealing. We assume that the amount of carbon for the two different surfaces is nearly the same because no carbon-containing species desorbs between 520 and 810 K. In our previous work, we took C 1s XPS spectra for the two different surfaces to verify the same carbon amount, but found a difference in C 1s binding energy (due to different chemical species; C₆H₅ and C). By dosing PA on the two different surfaces and taking TPD, here we elucidate a difference in hydrogenation of PA, and verify that PA associates with hydrogen of pre-adsorbed C₆H₅ to form styrene on Cu surface.

For the 104 amu TPD profiles, there is no peak in the 350 K region, i.e., no γ₄ desorption. Compared to the 102 amu profiles, the re-scaled (normalized) 104 amu profile overlaps

![Figure 1](image1.png)

**Figure 1.** The 102 and 104 amu TPD profiles for four dosing experiments: for multilayer PA dose (a) on clean Cu(111); (b) on pre-C₆H₄-covered Cu(111); (c) on pre-thicker C₆H₄-covered Cu(111); and (d) on pre-C-covered Cu(111). Inset: Selected 102 and 104 amu TPD regions before normalization. 104 amu: green shadowed, scaled by a normalization factor of (a) 4.5 ×, (b) 2.4 ×, (c) 2.6 ×, and (d) is scaled by 2.6 × for comparison with (c).

![Figure 2](image2.png)

**Figure 2.** Integrated TPD peak areas of 102 (γ₁, γ₂, and γ₁ + γ₂) and 104 amu (before normalization) displayed in Figure 1.
the 102 amu signal in the $\gamma_1$ region. But the normalization scaling factors differ: $4.5 \pm 0.1$ for clean Cu, $2.4 \pm 0.1$ for pre-$C_6H_6$-covered, and $2.6 \pm 0.1$ for pre-thicker $C_6H_6$-covered Cu(111) as seen in Figure 1. These ratios reflect changes in desorption of both PA and styrene, and indicate that while styrene and PA desorption are strongly coupled in the $\gamma_1$ region, the selectivity depends on the details of the local environment at the adsorbate-Cu interface.

For multilayer (2-3 ML) PA on clean Cu(111) shown in Figure 1(a), the 104 amu peak (green shadowed, scaled by $4.5 \times$) at 170 K is attributed to PA (or an impurity) based on the standard gas-phase mass spectrum of PA. On the other hand, the 104 amu peak at 410 K is $10 \times$ larger than expected from the gas-phase mass spectrum of PA. The excess intensity is then attributed to styrene ($C_6H_6$, 104 amu), a hydrogenation product of PA ($C_6H_{16}$, 102 amu). For the 102 (PA) and 104 amu (styrene) peaks at 410 K, the relative [styrene]/[PA] TPD ratio decreases with increasing the PA coverage up to 1.0 ML. At above 1.0 ML coverage of PA, the ratio is about $1/3.3$. We also checked a consecutive hydrogenation product $via$ CuH$_2$ (PA $\rightarrow$ C$_6$H$_6$ (styrene) $\rightarrow$ C$_8$H$_{16}$ (ethylbenzene), but no evidence of ethylbenzene (106 amu) was found. As a reference, the dehydrogenation of ethylbenzene to styrene occurs efficiently over catalysts.

It was reported that on Cu surface hydrogenation of acetylene with adsorbed atomic hydrogen is unlikely. Intuitively, we could assume that styrene with an ethylene group is also less likely for hydrogenation on Cu(111) with adsorbed atomic hydrogen. In Figure 1, the 102 amu peak at 170 K is assigned to multilayer PA. The two major peaks at 360 ($\gamma_2$) and 410 K ($\gamma_1$) are plausibly assigned to vertically aligned PA and parallel cross-bridged PA, respectively. The detailed adsorption geometry of PA on clean Cu(111) is fully discussed in our previous work.

For multilayer PA on pre-C$_6$H$_6$-covered Cu(111), the TPD is displayed in Figure 1(b). The multilayer TPD peak height is increased by $1.2 \times$, and there is broadening on its high temperature side at around 200 K. The $\gamma_2$ peak is intensified by $2.8 \times$, and shifted lower by 5 K. The $\gamma_1$ peak is suppressed by $0.65 \times$, and shifted lower by 15 K. In other words, the $\gamma_2/\gamma_1$ ratio is increased from 0.16 (for clean Cu) to 0.68, as seen in Figure 2. The total ($\gamma_1 + \gamma_2$) area of 102 amu is decreased by 0.94 $\times$. However, the 104 amu peak is increased by $1.2 \times$. The increase in $\gamma_2$ peak and the decrease in $\gamma_1$ peak can be explained as follows. Because the vertically aligned PA ($\gamma_2$) requires a narrower chemisorption space than compared to the parallel PA, as pre-covered adsorbates increase (or available chemisorption sites decrease) the vertically aligned PA could become more populated, relative to the parallel PA.

For multilayer PA on pre-thicker C$_6$H$_6$-covered Cu(111), the TPD is altered as follows (Figure 1(c)), compared to the previous TPD (Figure 1(b)). The 170 K peak is intensified (1.1 $\times$), and there is additional broadening on the high temperature side of this multilayer peak. The $\gamma_1$, but not $\gamma_2$, is further suppressed. That is, the $\gamma_2/\gamma_1$ ratio is further increased from 0.68 to 1.35, as seen in Figure 2. The 104 amu TPD peak is decreased by about $0.5 \times$, compared to Figure 1(b). The $\gamma_1$ peak is further shifted lower by 10 K while the $\gamma_2$ peak is stayed at the same position of 355 K.

For multilayer PA on pre-C-covered Cu(111), the TPD is shown in Figure 1(d). Unlike the pre-C$_6$H$_6$-covered surfaces (Figure 1(b) and 1(c)), there is a stronger shoulder on the high temperature side (210 K), and the $\gamma_1$ and $\gamma_2$ are a lot further suppressed. Interestingly and clearly, the $\gamma_2$ (102 amu) peak is not enhanced, compared to the pre-C$_6$H$_6$-covered Cu. As expected, but interestingly the 104 amu peak is considerably suppressed due to lack of hydrogen nearby PA. The intensity normalization scaling factor is $15 \times (104$ amu $\times 15 = 102$ amu). In Figure 1(d), the 104 amu is scaled by $2.6 \times$ (not $15 \times$) for comparison with that in Figure 1(c). For the TPD (not shown) of PA on Cu(111) pre-covered with considerable carbon impurities (uncharacterized), the $\gamma_1$ (102 amu) peak was completely suppressed, but the $\gamma_2$ peak was weakly observed. In addition, a significant 102 amu peak was found at 225 K, 15 K shift from the peak at 210 K shown in Figure 1(d).

We consider H$_2$ TPD profiles (Fig. 3). The background 2 amu signal in the UHV chamber is relatively large compared to the increases resulting from the PA surface chemistry.
From bottom to top of Figure 3, the 2 amu TPD results are shown as follows: (a) TPD of clean Cu(111) showing slow decline up to 625 K where the 2 amu signal rises as \( T \) increases to 810 K (a smooth dotted curve is drawn through this data and is used as a reference for the spectra); (b) multilayer PA on Cu(111); (c) multilayer PA on pre-C-H\(_x\)-covered Cu(111); and (d) multilayer PA on pre-C-covered Cu(111).

Comparing (b) with (a) and with (c) and (d) shows two interesting differences: (i) the local \( H \) desorption (hatched portion between 230 and 520 K) in (b) is absent in (a) and both (c) and (d), and (ii) the curve drawn through the blank (a) accounts for the slow decay observed in both (c) and (d) but does not account for the hatched portion of the rising 2 amu signal found for case (b). Evidently the species retained after TPD to 520 K, suppresses the surface chemistry giving rise to the steady evolution of \( H \) above the background at temperatures between 230 and 520 K. There is detectable \( H_2 \) desorption above background between 500 and 810 K in (b), (c) and (d). The \( H \) atoms on the phenyl ring may be removed over a broad temperature range and contribute to the slowly rising \( H_2 \) TPD intensity. For atomic hydrogen adsorbed on Cu(111), a TPD shows that hydrogen desorption occurs between 200 and 400 K.\(^{20}\) In Figure 3(b), the 2 amu desorption between 230 and 520 K appears to be due to association of adsorbed atomic hydrogens. In Figure 3(c) and (d), the absence of \( H_2 \) desorption below 500 K indicates that the adsorbed atomic \( H \) on Cu(111) is not sufficient for association reaction. Instinctively, as pre-covered adsorbates increase the adsorption sites for atomic hydrogen become less.

The styrene formation on Cu(111) at 410 K is a reaction-limited hydrogenation process governed by the available \( H \) atoms near PA.\(^{16}\) The styrene promptly desorbs once formed at 410 K because chemisorbed styrene on Cu(111) desorbs at 290 K.\(^{21}\) The source of \( H \) is either chemisorbed \( H \) or pre-adsorbed C-H\(_x\). On the basis of 2 amu profile discussed above, the \( H \) source for hydrogenation may be mostly from pre-adsorbed C-H\(_x\) because chemisorbed atomic \( H \) is not sufficient. In Figure 1(a), the 104 amu peak is predominantly seen at \( \gamma 1 \) position, not \( \gamma 2 \). For pre-covered C-H\(_x\), the 104 amu peak is increased by 1.2 \( \times \) although the 102 amu peak at \( \gamma 1 \) position is decreased by 0.65 \( \times \). This indicates that the possibility of hydrogenation increases when available \( H \) atoms near PA are abundant. The absence of 104 amu peak at \( \gamma 2 \) position could indicate that the \( \gamma 2 \) PA is not participated in the hydrogenation. If the \( \gamma 2 \) PA is participated in the hydrogenation, the reaction should proceed by step-wise reaction; step 1 followed by step 2, displayed in Figure 4.\(^{16}\) Intermediate 2 is formed both from \( \gamma 1 \) and \( \gamma 2 \) PA while intermediate 1 is formed only from \( \gamma 1 \) PA. In the step-wise reaction, the activation energy of step 2 should be much larger than that of step 1, but this is unlikely. Now, if we assume that the \( \gamma 1 \) PA is only participated in hydrogenation, and the step 1 and 2 occur simultaneously, in that way, we could explain why the 104 amu peak is absent at \( \gamma 2 \) position.

In Figure 5, we summarize our present study; hydrogenation reaction of PA on pre-C-H\(_x\)- and C-covered Cu(111) surfaces, and further discuss the reaction. In Figure 5, the \#1 and \#2 carbons of the flat-lying cross-bridged C=C (\( \gamma 1 \)) abstracts one hydrogen each from neighboring C-H\(_x\) to form styrene. If a PA is limited to use the hydrogens on the neighboring Cu atoms, two atomic hydrogens are required for ten Cu (gray colored) atoms; 2H/10Cu. For a vertically aligned PA (\( \gamma 2 \)) where the \#1 carbon is bridged on two adjacent Cu atoms, the \#1 carbon abstracts two hydrogens to form styrene. In this case, two neighboring hydrogens are required for eight Cu (gray) atoms; 2H/8Cu. For another \( \gamma 2 \) where the \#1 carbon is bonded to atop Cu atom (Cu=C(\#1) =CH–Ph), two hydrogens are required for six neighboring Cu atoms; 2H/6Cu. That is, compared to \( \gamma 1 \), the \( \gamma 2 \) requires more neighboring hydrogens per unit area. As the pre-adsorbed C-H\(_x\) increases, the chemisorption site of parent PA decreases, but the chance of hydrogen reaction for a chemisorbed PA will increase; as discussed, the scaling factor (shown in Figure 1) dramatically changes from 4.5 \( \times \) to 2.4 \( \times \). When the Cu surface is pre-covered by amorphous atomic carbon (achieved by annealing to 810 K in Figure 1(d)), styrene formation is dramatically reduced due to lack of pre-adsorbed hydrogen nearby PA. As the coverage of pre-adsorbed C-H\(_x\) increases the 104 amu intensity near \( \gamma 2 \) position increases, but not significantly. This indicates that the hydrogenation using \#1 C of \( \gamma 2 \) PA less likely occurs, compared to \#1 C (or \#2 C) of \( \gamma 1 \) PA. This observation is very similar to the hydrogenation of ethylene; the hydrogenation

![Figure 4](image-url) Plausible two-step hydrogenation processes of PA (\( \gamma 1 \) and \( \gamma 2 \)) on pre-C-H\(_x\)-covered Cu(111) surface.\(^{16}\)

![Figure 5](image-url) Schematics of hydrogenation reaction processes of PA (\( \gamma 1 \) and \( \gamma 2 \)) on pre-C-H\(_x\)- and C-covered Cu(111) surfaces.
of flat-lying ethylene (H2C(adt-Cod)H2) is predominant, compared to that of vertically aligned ethylidyne (C(adt-Cod)H).22 As a reference, similarly, the parallel γ1 PA is highly reactive to pre-adsorbed atomic oxygen while the vertically aligned γ2 PA is less impacted for chemical reaction.23

Summary

The hydrogenation of PA (C8H8, 102 amu) on pre-adsorbate-covered Cu(111) has been studied by temperature-programmed desorption. Two different pre-adsorbate-covered Cu(111) surfaces are achieved by annealing of multilayer PA on Cu(111) to 520 and 810 K, respectively. We have proved that chemisorbed PA with an acetylene group associates with hydrogen of pre-adsorbed C3H6 to form styrene (104 amu), a major hydrogenation product. The styrene desorption is increased on pre-C3H6-covered Cu(111) surface while that is dramatically decreased on pre-C-covered surface. No ethylbenzene forms on the surface by hydrogenation. Two major PA (102 amu) desorption peaks at 360 K (γ2) and 410 K (γ1) are assigned to chemisorbed vertically aligned PA and flat-lying cross-bridged PA, respectively (J. Phys. Chem. C 2007, 111, 5101). The 102 amu TPD peak at 360 K (γ2) is increased while that at 410 K (γ1) is decreased with increasing pre-covered C3H6 on Cu (111) surface before dosing PA. However, for pre-C-covered surface, the γ2 peak is clearly not enhanced. The cross-bridged PA (γ1) may dominantly associate with hydrogen of pre-adsorbed C3H6 to form styrene that promptly desorbs at 410 K, while the vertically aligned structure (γ2) is less likely participated in hydrogenation reaction.

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References

17. The measured fragmentation pattern of gas phase PA: 102 amu (1.00), 76 amu (0.26), 101 amu (0.026), 104 amu (0.015), 106 amu (0.0024), and 91 amu (0.0085). [NIST] http://webbook.nist.gov/chemistry/ (22 Nov. 2010)