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Sum Frequency Generation Vibrational Spectroscopic and High-Pressure Scanning Tunneling Microscopic Studies of Benzene Hydrogenation on Pt(111)

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Abstract: Sum frequency generation (SFG) vibrational spectroscopy and high-pressure scanning tunneling microscopy (HP-STM) have been used in combination for the first time to study a catalytic reaction. These techniques have been able to identify surface intermediates in situ during benzene hydrogenation on a Pt(111) single-crystal surface at Torr pressures. In a background of 10 Torr of benzene, STM is able to image small ordered regions corresponding to the c($2\sqrt{3} \times 3$)*rect* structure in which each molecule is chemisorbed at a bridge site. In addition, individual benzene molecules are also observed between the ordered regions. These individual molecules are assumed to be physisorbed benzene on the basis of the SFG results showing both chemisorbed and physisorbed molecules. The surface becomes too mobile to image upon addition of hydrogen but is determined to have physisorbed and chemisorbed benzene present by SFG. It was spectroscopically determined that heating the platinum surface after poisoning with CO displaces benzene molecules. The high-coverage pure CO structure of ($\sqrt{19} \times \sqrt{19}$)*R*23.4° imaged with STM is a verification of spectroscopic measurements.

1. Introduction

High-pressure scanning tunneling microscopy (HP-STM) and sum frequency generation (SFG) vibrational spectroscopy have been widely used to study high-pressure reactions by means of atomically resolved images of surfaces and chemical information of adsorbates.[1−7] However, these techniques have never been combined to investigate catalytic reactions. Using these techniques to study benzene hydrogenation leads to better understanding of surface adsorbate chemical composition, bonding, and structure during reaction.

Traditionally, benzene has been studied at low pressures (<10^{-6} Torr) and low temperatures (<300 K), which are far removed from catalytically relevant conditions. Briefly, benzene has been shown to preferentially adsorb to bridge sites at low coverages and to 3-fold hollow sites at high coverages by STM[8]

and density functional theory (DFT).[9] Electron energy loss spectroscopy (EELS)[10−12] studies have shown two distinct vibrational signatures for low and high coverages, chemisorbed and physisorbed benzene. Taken together, the various techniques show that benzene preferentially adsorbs to bridge sites in the low-coverage limit, whereas for high coverages adsorption onto 3-fold hollow sites is observed.[13] Chart 1 depicts the chemisorbed species, which is thought to be dienyl in nature. Physisorbed benzene is thought to be flat-lying by EELS[12,14] and near-edge X-ray absorption spectroscopy (NEXAFS).[15]

In this study, SFG vibrational spectroscopy, HP-STM, and reaction turnover studies are used for the first time to investigate and identify the surface species present during benzene hydrogenation (10 Torr of benzene) in the presence of excess hydrogen (100 Torr) and in a range of temperatures (300−440 K). This reaction is also studied by poisoning the platinum surface with 5 Torr of CO. The electric dipole approximation forbids centrosymmetric media and isotropic gases from appearing in the SFG spectrum. Since bulk platinum has a center of inversion, its contribution to the SFG signal is negligible.

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Chart 1. Schematic Diagram of Dienyl Chemisorbed Benzene (C_6H_6) Intermediate
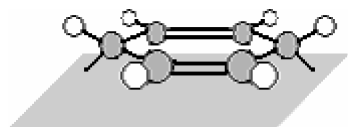
This symmetry is broken at the surface, allowing for a surface-specific signal. For these reasons, SFG is an ideal tool to probe single-crystal surfaces for chemical functionalities at high pressures. HP-STM has the ability to monitor adsorbates and metal atoms, provided their mobility occurs at speeds comparable to or less than the scan rate of approximately 10 μm/s. The unique ability to detect surface dynamics complements the time-averaged spectroscopic information obtained from SFG. HP-STM is also capable of accessing structure and bonding information.

Our findings show that both physisorbed and chemisorbed benzene are present on the surface in a background of 10 Torr of benzene by SFG. Small ordered regions are observed by STM and identified as having the $c(2\sqrt{3} \times 3)rect$ structure, in which each molecule is chemisorbed at a bridge site. Individual benzene molecules are also observed between the ordered regions that likely correspond to the physisorbed benzene identified by SFG. Adding hydrogen to the system mobilizes the surface by STM. SFG is able to detect physisorbed and chemisorbed benzene. Heating the platinum surface after poisoning with CO displaces benzene molecules evidenced by SFG. STM is able to verify this after imaging the $(\sqrt{19} \times \sqrt{19})$-$R23.4°$ structure after cooling to room temperature, corresponding to the high-coverage pure CO structure.

2. Experimental Section

2.1. Sum Frequency Generation Vibrational Spectroscopy. All SFG experiments were carried out in a high-pressure/ultrahigh-vacuum (HP/UHV) system on a prepared Pt(111) single-crystal surface. The HP/UHV system consists of a UHV chamber operating at a base pressure of 2×10^{-9} Torr and a HP cell isolated from the UHV chamber by a gate valve. The UHV chamber is equipped with an Auger electron spectrometer (AES), a quadrupole mass spectrometer (QMS), and an Ar^+ ion sputter gun. Two CaF_2 conflat windows on the HP cell allow transmission of infrared (IR), visible (VIS), and sum frequency radiation for SFG experiments. The HP cell is equipped with a recirculation loop that includes a diaphragm pump and a septum for gas chromatographic analysis. The reactant and product gases are constantly mixed via a recirculation pump, while kinetics data are acquired by periodically sampling the reaction mixture and measuring the relative gas-phase composition with gas chromatography (GC) (FID detection and 0.1% AT-1000 on Graphpac GC 80/100 packed column (Alltech)).

The Pt(111) crystal was cleaned by sputtering with Ar^+ ions (1 keV) for 20 min, heating to 1123 K in the presence of 5×10^{-7} Torr of O_2 for 2 min, and then annealing at 1123 K for 2 min. AES and low-energy electron diffraction (LEED) were used to verify the cleanliness of the Pt(111) surface after several cleaning cycles. The Pt(111) sample was then transferred into the HP cell for SFG reaction studies. Benzene ($\geq$99.0%, EM Science) was purified by several freeze−pump−thaw cycles before introduction into the HP cell. Prior to the experiment, benzene was checked for impurities by means of GC. Such impurities were below 0.5% and consisted of mostly light alkanes below C_6. During poisoning experiments, CO was introduced after the Pt(111) single crystal was exposed to benzene and hydrogen.

A Nd:YAG laser (1064 nm fundamental having a 20 ps pulse width operating at a 20 Hz repetition rate) was used to create a tunable IR (1800−4000 cm^{-1}) and a second harmonic VIS (532 nm) beam. The VIS beam (200 μJ) and the IR (200 μJ) beams were spatially and temporally overlapped on the Pt(111) surface, with incident angles of 55° and 60° with respect to the surface normal. All spectra were taken using a ppp polarization combination (SFG, VIS, and IR beams were all p-polarized). The generated SFG beam was sent through a monochromator, and the signal intensity was detected with a photo-multiplier tube and a gated integrator as the IR beam was scanned over the spectral range of interest. Spectra were curve-fit using a previously reported procedure[16,17] to a form of the equation

$$I_{\text{SFG}} \propto |\chi_{\text{NR}}^{(2)} \, e^{i\phi_{\text{NR}}} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \, e^{i\gamma_q}|^2 \qquad (1)$$

where $\chi_{\text{NR}}^{(2)}$ is the nonresonant nonlinear susceptibility, $e^{i\phi_{\text{NR}}}$ is the phase associated with the nonresonant background, A_q is the strength of the qth vibrational mode, ω_{IR} is the frequency of the incident infrared laser beam, ω_q is the frequency of the qth vibrational mode, Γ_q is the natural line width of the qth vibrational transition, and $e^{i\gamma_q}$ is the phase associated with the qth vibrational transition. Detailed descriptions of the HP/UHV system and SFG measurement can be found elsewhere.[1,5,18−21]

2.2. High-Pressure Scanning Tunneling Microscopy. STM experiments were performed in a high-pressure, high-temperature scanning tunneling microscope that has been described in detail elsewhere.[22] The system combines a UHV surface analysis/preparation chamber with a variable-temperature (298−675 K) and variable-pressure ($10^{-10}-10^3$ Torr) scanning tunneling microscope from RHK (model VT-UHV 300). The base pressure of the system was 1×10^{-10} Torr, with a background mostly made up of H_2, CO, and H_2O. Using three gate valves, the STM chamber can be isolated from the rest of the system and filled with any gas mixture up to a total pressure of 1 atm.

The sample was a platinum single crystal of (111) orientation from Matek Corp. with a miscut angle of <0.3°. Before each experiment, the sample was sputtered in 5×10^{-6} Torr of Ar for 15 min at an ion energy of 500 eV and current of 4 μA. After sputtering, the sample was heated with an electron beam to 1073 K for 10 min. The sample was then sputtered again and annealed at 1073 K for 4 min before being transferred to the STM chamber. Sample composition was monitored using AES and its cleanliness/flatness checked with STM prior to gas introduction.

During experiments, the STM chamber was isolated from the rest of the system while combinations of benzene, hydrogen, argon, and carbon monoxide were introduced. The hydrogen, argon, and CO were of ultrahigh-purity grade, while the benzene (>99.5%, Aldrich) was further purified by freeze−pump−thaw cycles prior to use. If the experiment involved CO, it was introduced after the sample had reached experimental temperature. A 150 W quartz projector bulb positioned just below the sample without making mechanical contact accomplished sample heating. A type K thermocouple, spot-welded to the side of the crystal, monitored the sample temperature. The sample was always allowed to equilibrate at least 5 min prior to imaging. Images were taken with electrochemically etched tungsten tips, following the technique described by Klein et al.[23] STM settings during image acquisition were $I = 0.05-0.2$ nA and $V = 50-100$ mV. MKS Instrument Baratrons were used, model 122A for 0.1 mTorr−10 Torr and model 722A for experiments exceeding 10 Torr.

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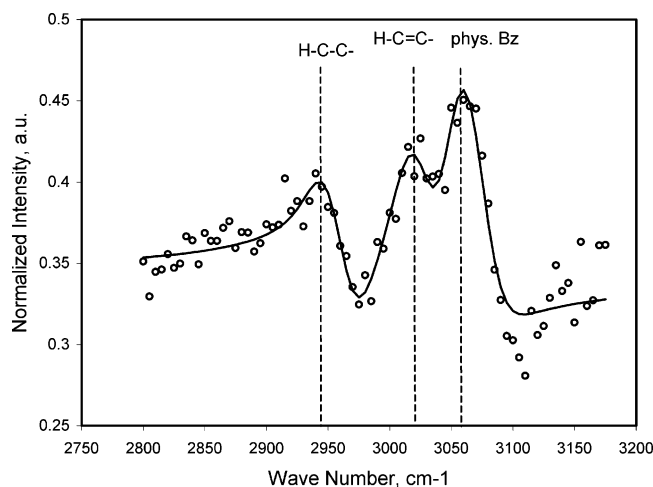(23) Klein, M.; Schwitzgebel, G. *Rev. Sci. Instrum.* **1997**, *68*, 3099.

Figure 1. SFG spectra of surface species on Pt(111) under 10 Torr of benzene at 300 K. H−C−C−, vinylic (H−C=C−), and physisorbed benzene (phys. Bz) bands are identified. Markers represent experimental data, and solid lines represent the curve fits.

3. Results and Discussion

3.1. In Situ SFG Vibrational Spectroscopy and HP-STM of Surface Species Present on Pt(111) at 300 K under 10 Torr of Benzene. The SFG spectrum of the surface species adsorbed on Pt(111) at 10 Torr of benzene at 300 K is presented in Figure 1. Three peaks are observed at 2945, 3030, and 3060 cm^{-1}. The peak at 3060 cm^{-1} has been assigned to physisorbed benzene.[2,11] Previous studies using EELS,[11,12] NEXAFS,[15] reflection/absorption infrared spectroscopy (RAIRS),[24] and DFT[13,25] have shown that benzene adsorbs parallel to the surface on platinum. Since the molecule physisorbs intact, the six carbons and hydrogens are assumed to be roughly equivalent, resulting in only one peak in the C−H stretching region as observed by EELS.[11,12] This assignment can be further substantiated by referencing the aromatic C−H stretch at 3068 cm^{-1} present in the gas-phase IR spectrum.[11]

Two peaks centered around 2960 and 3020 cm^{-1} have been observed by infrared/high-resolution electron energy loss spectroscopy (IR/HREELS)[12,14] for low coverages (0.2 L, 1 Langmuir (L) = 10^{-6} Torr·s) of benzene. Thomas et al.[12] have suggested that the peak at 2960 cm^{-1} arises from an sp^3-hybridized carbon. The absence of modes at 1815 and 1960 cm^{-1} led Thomas et al.[12] to propose a structure of a dienyl nature for chemisorbed benzene (see Chart 1). Grassian and Muetterties have also proposed a similar chemisorption structure.[14] The proposed structure has two double and four single carbon−carbon bonds. The singly bonded carbons are bound to the platinum surface, resulting in the sp^3-hybridized character of the vibrational signature. The apparent simultaneous growth and decay of both the 2945 and 3030 cm^{-1} peaks with variation of temperature observed by SFG[2] corroborates this assignment. Hence, the modes in Figure 1 have been assigned as follows: ν(H−C−C−) = 2945 cm^{-1}, ν(C−H)(vinylic) = 3030 cm^{-1}, and ν(C−H)(aromatic) = 3060 cm^{-1}. The absence of a symmetric CH$_2$ stretch in Figure 1 indicated that the adsorbate is some C$_6$H$_6$ or more dehydrogenated species (e.g., polyaromatics).

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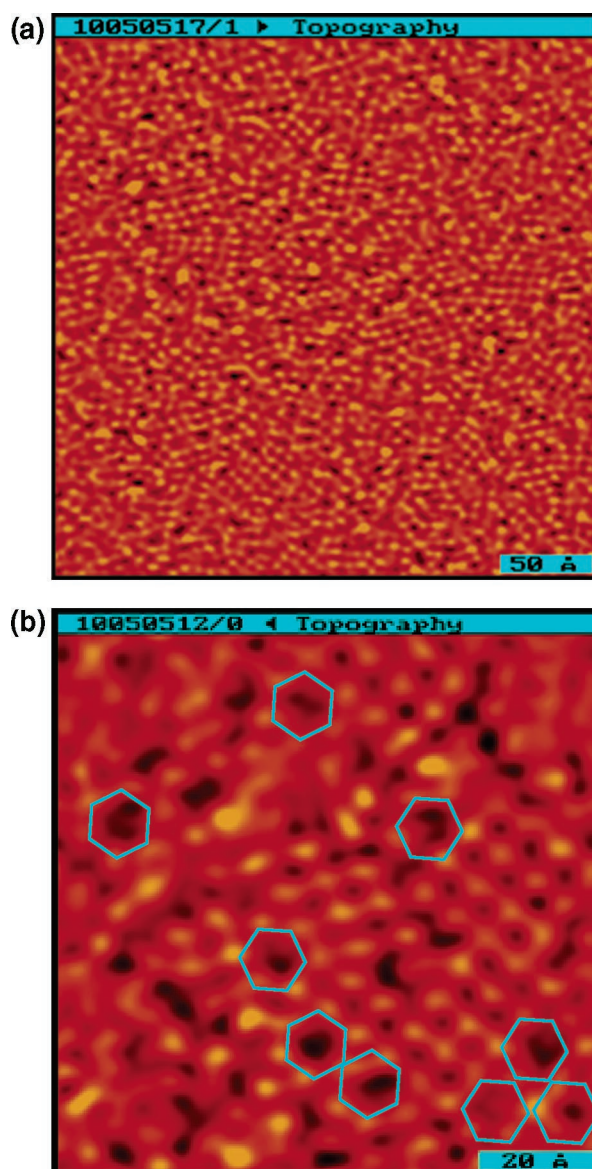
Figure 2. STM images of Pt(111) in the presence of 10 Torr of benzene at 298 K with a scan area of (a) 300 Å × 300 Å and (b) 95 Å × 95 Å. Hexagons represent six benzene molecules forming a hexagonal ring with an apparently hollow center, most likely containing a weakly bound physisorbed species.

Imaging the surface with HP-STM reveals a surface covered with immobile adsorbed benzene, as shown in Figure 2. The surface is largely disordered, with patches of short-range order composed of 15−30 adsorbed molecules. Previous studies of Pt(111) electrodes in a benzene solution by Yau et al.[26] yields very similar results, with small ordered regions separated by disordered areas. These small patches appear to be the c(2√3 × 3)*rect* structure reported by Yau et al.,[26] in which each molecule is chemisorbed at a bridge site. Between the patches of order, easily resolved individual benzene molecules are also bound, which are likely bound to the 3-fold hollow site and are responsible for the physisorbed species observed in the SFG spectrum (see Figure 1). In addition, several six-member hexagonal rings (see Figure 2a) form, in which all benzene molecules are adsorbed at 2-fold bridge sites.[26] Yau et al.[26] concluded that the "chemisorbed benzene at 2-fold sites is

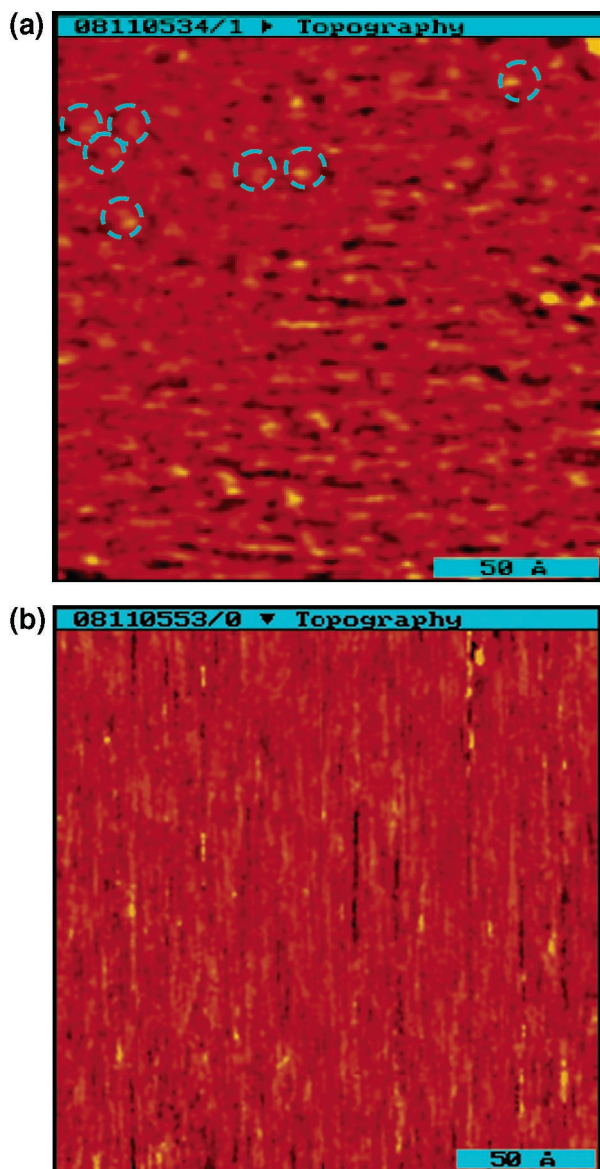(26) Yau, S.-L.; Kim, Y.-G.; Itaya, K. *J. Am. Chem. Soc.* **1996**, *118*, 7795.

Figure 3. 200 Å × 200 Å STM images of Pt(111) in the presence of 10 Torr of benzene, 100 Torr of H_2, and 650 Torr of Ar (a) at 298 K and (b) heated to 353 K. Rings represent adsorbed benzene.

Figure 4. Temperature-dependent SFG spectra of surface species on Pt-(111) under 10 Torr of benzene and 100 Torr of H_2 in the range of 300–440 K. The top SFG spectrum was taken after the metal surface was cooled from 440 to 300 K. H−C−C−, vinylic (H−C=C−), and physisorbed benzene (phys. Bz) bands are identified. Markers represent experimental data, and solid lines represent the curve fits.

greatly distorted toward the boatlike structure" and that these structures appear to be $(\sqrt{21} \times \sqrt{21})R10.9°$. These hexagonal rings have an apparently hollow center that most likely contains a weakly bound physisorbed species that is difficult to image due to its shorter residence time, as concluded by Yau et al.,[26] who found that "an additional benzene molecule can be squeezed into the unit cell". Furthermore, Saeys et al.[13] found through DFT studies that the tilted geometry is energetically feasible. Zebisch et al.[27] were able to observe the tilted adsorption of benzene on Pt(110) 1 × 2 with angle-resolved UV photoemission (ARUPS) and NEXAFS.

3.2. Temperature Dependence of the Major Surface Species under 10 Torr of Benzene and 100 Torr of H_2 As Studied by HP-STM and SFG Vibrational Spectroscopy. Upon the addition of 100 Torr of H_2 and 630 Torr of Ar, the surface changes dramatically, as evidenced by STM (see Figure
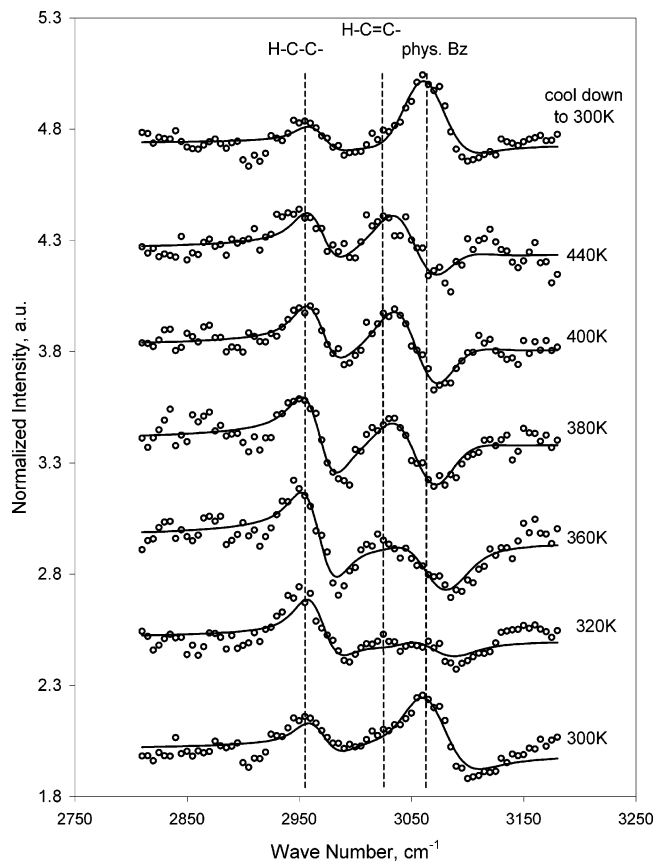
3a). The patches of ordered benzene disappear, and only a few isolated benzene molecules are visible on the largely mobile adsorbate layer. A few of the benzene molecules that can still be imaged are highlighted in Figure 3a. This is not entirely surprising, as excess hydrogen is known to weaken the surface bonding of adsorbed organic species and increase their mobility.[4] When the surface is heated to 353 K, all surface ordering of the resolved adsorbed molecules is lost as the adsorbed monolayer becomes too mobile to be imaged by our STM, as shown in Figure 3b.

The surface chemistry of adsorbed benzene in the presence of excess H_2 at elevated temperatures, not visible by STM, can be studied by SFG vibrational spectroscopy. Figure 4 shows the SFG spectra of 10 Torr of benzene and 100 Torr of H_2 on Pt(111) as the surface temperature is varied from 300 to 440 K. Like the spectrum of 10 Torr of benzene, these spectra exhibit three bands at 2945, 3030, and 3060 cm^{-1}. These bands are attributed to the chemisorbed and physisorbed species, as discussed in the previous section. Increasing the temperature to 320 K desorbs the physisorbed benzene, leaving the chemisorbed species as the dominant surface species. Chemisorbed benzene reaches a maximum surface coverage at 400 K, based on the SFG signal intensity reaching a maximum at that temperature. Cooling the surface to 300 K allows physisorbed benzene to readsorb and shows that a carbonaceous layer does not poison the surface.

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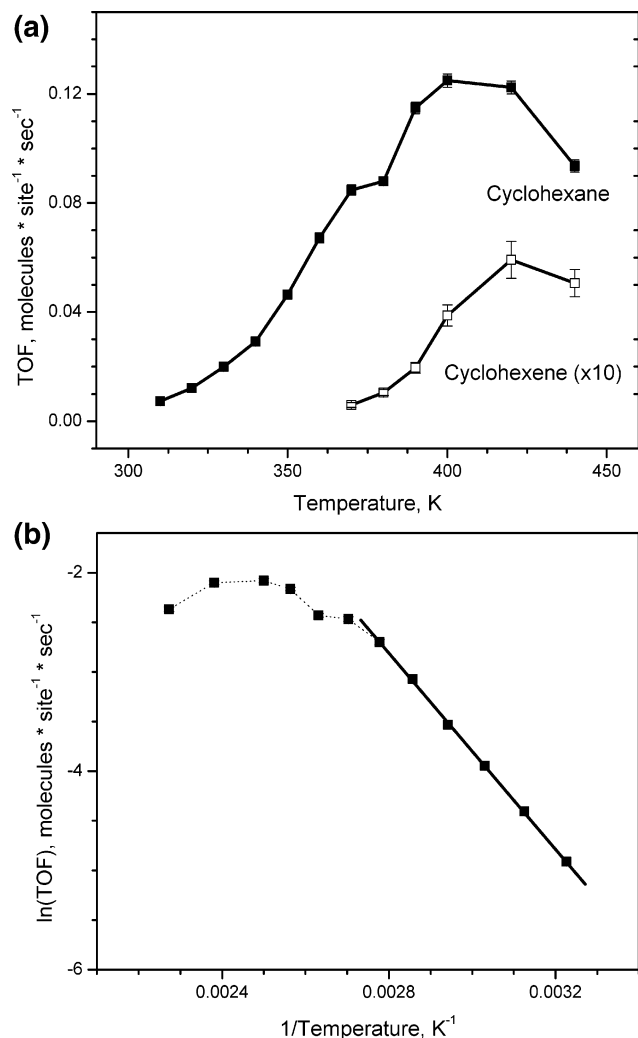
(a)

(b)

Figure 5. (a) Turnover rates (TORs) for the hydrogenation to cyclohexane and cyclohexene under 10 Torr of benzene and 100 Torr of H_2 and (b) Arrhenius plot for the TORs of cyclohexane. Apparent activation energy is 9.8 ± 0.1 kcal/mol for cyclohexane formation. The non-Arrhenius behavior above 370 K is explained in terms of changes in the surface coverage of the adsorbates. The dotted line was drawn as a visual aide.

3.3. Turnover Rates and Activation Energies To Form Cyclohexane and Cyclohexene under 10 Torr of Benzene on Pt(111) in the Presence of 100 Torr of H_2. Figure 5 displays the kinetic studies carried out in the presence of 10 Torr of benzene and 100 Torr of H_2 using gas chromatography detection over the 310−440 K temperature range. Estimated turnover frequencies (TOFs) [molecules·Pt site^{-1}·s^{-1}] are shown in Figure 4a, giving production of cyclohexane and cyclohexene as a function of temperature. The corresponding Arrhenius plot of the TOFs for cyclohexane is given in Figure 4b. Above 370 K, the observed TOFs for cyclohexane deviate from the linear Arrhenius regression line. This is explained by a change in the surface coverage of the adsorbed species, as previously discussed.[1] The apparent activation energy for the hydrogenation to cyclohexane is 9.8 ± 0.1 kcal/mol. A maximum of cyclohexane turnover is observed at 400 K, corresponding to the maximum surface coverage of chemisorbed benzene, as seen with SFG vibrational spectroscopy. In a previous study, Bratlie et al.[2] concluded that chemisorbed benzene is a reactive surface intermediate critical to benzene hydrogenation. This conclusion is further supported by our kinetic and vibrational studies.
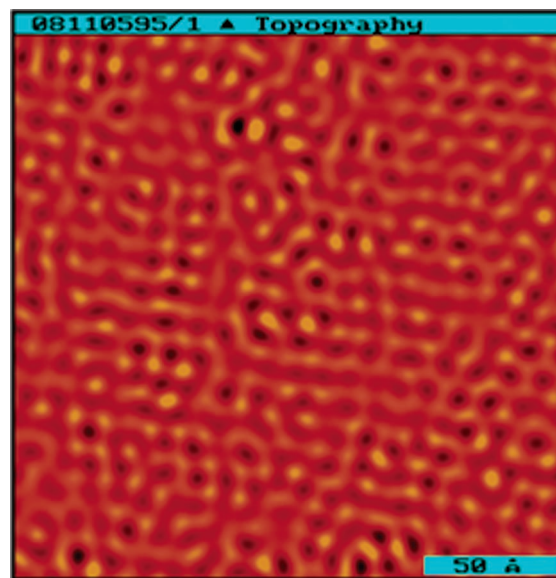
Figure 6. 200 Å × 200 Å STM image of Pt(111) in the presence of 10 Torr of benzene, 100 Torr of H_2, and 630 Torr of Ar heated to 353 K, 5 Torr of CO added, and cooled to 298 K. The high-coverage pure CO structure corresponds to the ($\sqrt{19} \times \sqrt{19}$)R23.4° structure. All benzene adsorbates have been displaced by the strongly bound and closely packed CO molecules.

Perhaps the most noticeable feature observed in Figure 5a is the dip in cyclohexane formation at 380 K. This feature has been attributed to the onset of cyclohexene formation, which is initially observed at 370 K but significantly increases with surface temperature. Previous studies[2] have ascribed this to the larger sticking coefficient of cyclohexene (0.2[28]) as compared to that of cyclohexane (<0.1[29]). This larger sticking coefficient allows for further hydrogenation of cyclohexene.

3.4. Major Surface Species Present under 10 Torr of Benzene and 100 Torr of H_2 after Poisoning with 5 Torr of CO As Studied by HP-STM and SFG Vibrational Spectroscopy: Temperature Effects. Previous studies by Ogletree et al.[30] show that adsorbing CO molecules first creates a very large work function for the hydrocarbon to overcome in order to adsorb on the surface. For this reason, CO was introduced after benzene and H_2 addition. The presence of CO has no effect on the surface structure of the system as observed by STM at 353 K. Again, this is attributed to the fact that, although CO is now present on the surface, its high mobility makes imaging with STM difficult. This is also observed previously under lower pressure conditions.[4,8] When the mobile CO dominated surface is cooled to 298 K, the increase in CO surface coverage forms an immobile surface structure, as can be seen in Figure 6. This high-coverage pure CO structure was first reported by the Besenbacher group[31] and observed in our laboratory as well.[3] The structure corresponds to the ($\sqrt{19} \times \sqrt{19}$)R23.4° structure, with a total coverage of ~0.7 monolayer. As observed with STM, benzene no longer remains on the surface, as all physisorbed and chemisorbed species are displaced by the more strongly bound and more closely packed CO molecules.

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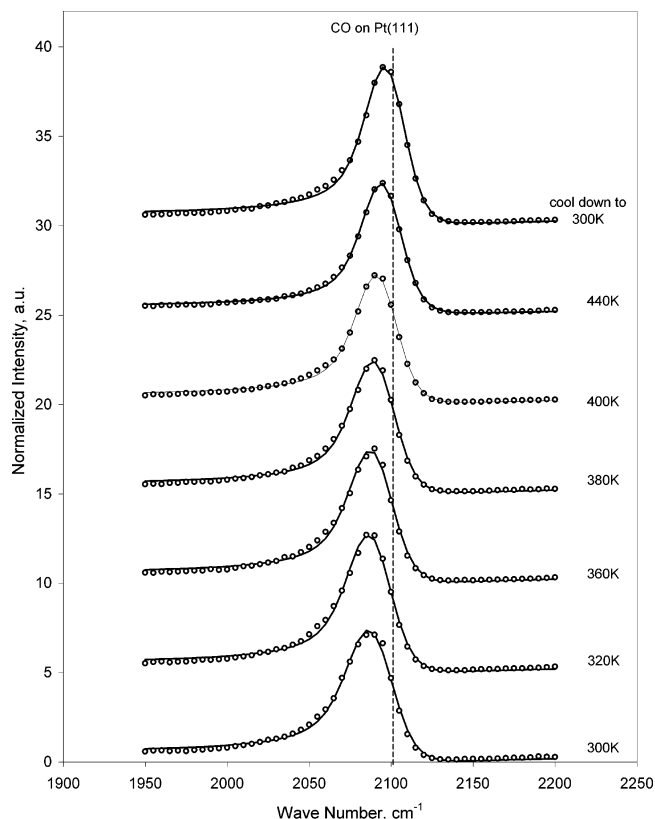
Figure 7. Temperature-dependent SFG spectra of surface species on Pt-(111) under 10 Torr of benzene, 100 Torr of H_2, and 5 Torr of CO in the range of 300−440 K. The top SFG spectrum was taken after the metal surface was cooled from 440 to 300 K. The band for the C−O stretch adsorbed on clean Pt(111) is identified. Markers represent experimental data, and solid lines represent the curve fits.

Figure 8. CO vibrational resonance frequency, ω_{CO}, plotted against the metal surface temperature. The solid line was drawn as a visual aide.

Figure 9. Temperature-dependent SFG spectra of surface species on Pt-(111) under 10 Torr of benzene, 100 Torr of H_2, and 5 Torr of CO in the range of 300−440 K. The top SFG spectrum was taken after the metal surface was cooled from 440 to 300 K. H−C−C−, vinylic (H−C=C−), and physisorbed benzene (phys. Bz) bands are identified. Markers represent experimental data, and solid lines represent the curve fits.

To understand how CO affects adsorbates at elevated temperatures, SFG is used to monitor the system under identical conditions. McCrea et al.[32] have reported that CO adsorbed on clean Pt(111) has a C−O stretch at 2094 cm^{-1}. Upon CO coadsorption with benzene and H_2, the C−O stretch appears at 2090 cm^{-1}, as given in Figure 7. The red-shifting of the C−O stretch results from a weakening of the C−O bond, which may be due to an interaction with the adsorbed benzene. According to Jasen et al.,[33] the red-shift results from a "charge transfer from benzene via the substrate to CO", which strengthens the CO−Pt bond. Increasing the surface temperature to 440 K blue-shifts the C−O band to 2094 cm^{-1} (illustrated in Figure 8), which remains as the surface is cooled to 300 K, displaying the irreversibility of the system. Presumably, the blue-shift of the C−O band results from displacement of the benzene molecules, as observed with STM.

SFG vibrational spectroscopy is also used to probe this system in the C−H stretching region, as shown in Figure 9. Coadsorption of CO with benzene and H_2 reveals similar spectra with and without H_2 at 300 K (see Figures 1 and 4). Heating the surface led to the eventual desorption of physisorbed and chemisorbed benzene. Neither of these surface species readsorb after cooling the surface to 300 K. On the basis of the results from STM and the SFG spectra of the C−O stretching region,
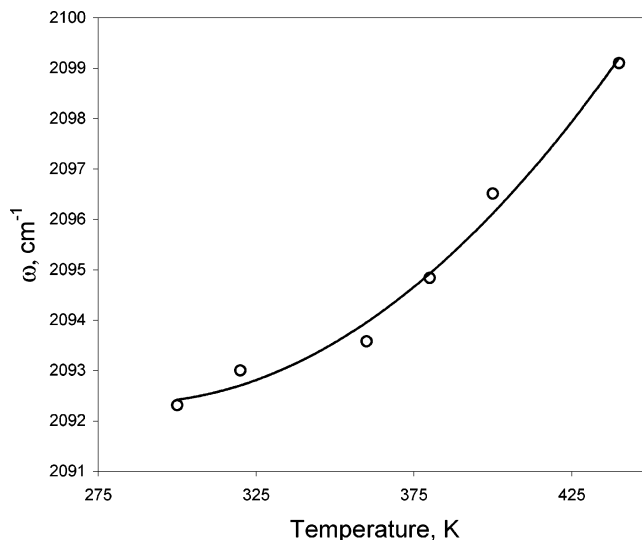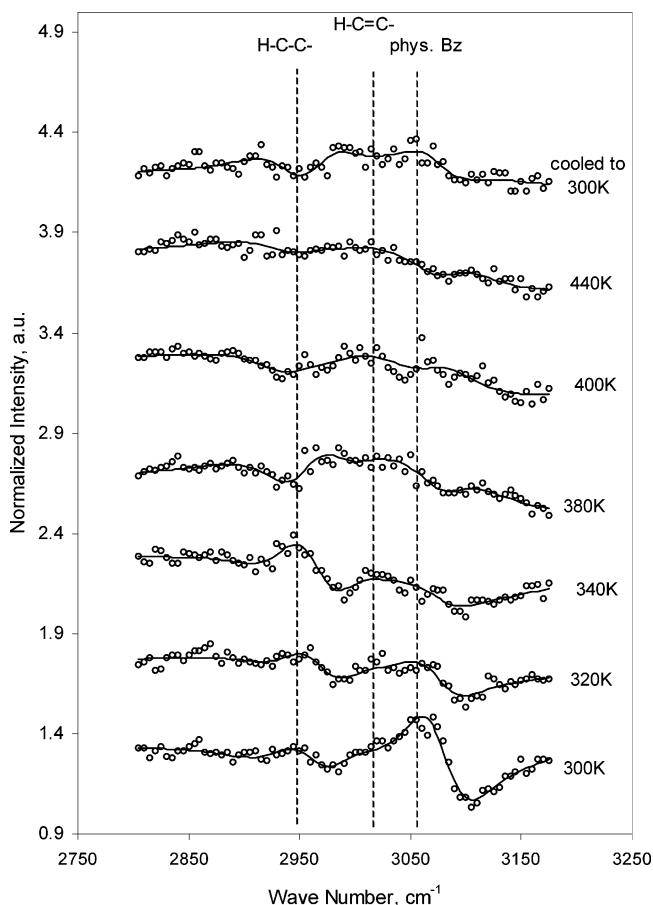
we conclude that CO displaces any hydrocarbon previously on the surface. Furthermore, since the C−O vibration after cooling from 440 to 300 K is so similar to that of CO on clean platinum, we assert that benzene desorbs intact and does not dehydrogenate to form a carbonaceous layer.

(32) McCrea, K. R.; Parker, J. S.; Somorjai, G. A. *J. Phys. Chem. B* **2002**, *106*, 10854.
(33) Jasen, P. V.; Brizuela, G.; Padin, Z.; Gonzalez, E. A.; Juan, A. *Appl. Surf. Sci.* **2004**, *236*, 394.

4. Conclusions

The chemical composition and adsorption structures of the surface species are measured during benzene hydrogenation on Pt(111) by SFG vibrational spectroscopy and HP-STM. Small ordered regions corresponding to the $c(2\sqrt{3} \times 3)rect$ structure, in which each molecule is chemisorbed at a bridge site, are imaged in a 10 Torr background of benzene. Individual physisorbed benzene molecules are observed between these ordered regions. Several six-member hexagonal rings with a seemingly hollow center are imaged. The hollow center most likely contains a physisorbed species. Upon the addition of hydrogen, SFG is necessary to characterize the surface, as it has become too mobile to image. Both physisorbed and chemisorbed benzene are present under 100 Torr of hydrogen. Raising the temperature desorbs physisorbed benzene and leaves the chemisorbed species on the surface. Spectroscopic evidence shows that poisoning the reaction with CO displaces the adsorbed benzene molecules. This assertion is validated by the $(\sqrt{19} \times \sqrt{19})R23.4°$ structure imaged after cooling the surface, which corresponds to pure CO at high coverages.

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