Catalytic Cyclopropane Hydrogenation on Platinum(111) Using In Situ Soft X-ray Methods[†]

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As part of a continuing program focused on the role of hydrogen in catalytic reactions, cyclopropane hydrogenation on the Pt(111) surface has been characterized using in situ soft X-ray studies above the carbon K edge. In situ soft X-ray methods provide interesting new information regarding concentrations, stoichiometries, bonding, and reactivities of adsorbed carbon-containing species under reaction conditions. At low temperature, cyclopropane is weakly adsorbed and tilted up from the Pt(111) surface. The saturation coverage is 4.4×10^{14} molecules/cm^2 at 100 K. Catalytic hydrogenation of cyclopropane to form propane is observed during batch reactivity studies in the 350 K range. No methane or ethane products are observed. Approximately 2.9×10^{14} C$_3$ molecules/cm^2 of adsorbed carbonaceous species are observed on the surface at 350 K under reaction conditions. The concentration of these species decreases above 350 K in excess hydrogen. In situ isothermal reactivity studies in hydrogen near 350 K indicated that a significant fraction of these species can be removed from the surface with a thermal activation energy of 15.2 kcal/mol. Taken together the observation of catalytic propane formation and the estimated activation energy suggests that the surface species are directly involved in propane formation. In situ characterization of this species, using soft X-ray C–H intensities to determine stoichiometry, indicates that a C$_3$H$_6$ species is dominant up to 320 K. In situ glancing and normal spectra taken at 320 K indicate that the C$_3$H$_6$ species is a platinacylobutane intermediate adsorbed in an upright configuration relative to the surface. Increasing temperature to 350 K under reaction conditions increases the average C–H stoichiometry to C$_3$H$_7$. This hydrogen addition suggests formation of adsorbed propyl in the 350 K temperature range. Taken together these experiments indicate that the dominant mechanism for C–C bond breaking is associated with insertion of the Pt surface into the adsorbed cyclopropane reactant to form a metallocycle intermediate. This metallocycle is strongly bound and stable up to 320 K in large excesses of hydrogen. With increasing temperature this C$_3$ platinacyclobutane intermediate is hydrogenated to form propane in the 350 K range. Observation of a hydrogenated C$_3$H$_7$ intermediate suggests that propane formation may involve sequential hydrogen addition and a transient propyl intermediate.

Introduction

Hydrogen plays an important role in a wide range of catalytic reactions involving organic species on metal surfaces. As part of our efforts to understand the role of hydrogen in C–C bond activation, we have recently characterized cyclopropane hydrogenation on several active metal surfaces including the Pt(111) surface. Coadsorbed hydrogen and cyclopropane generally do not react in the absence of gas-phase cyclopropane because cyclopropane desorbs before reacting. However, on both Ni and Pt surfaces, adsorbed propyl formed by reaction with gas-phase hydrogen radicals can be readily hydrogenated by coadsorbed hydrogen below 200 K.[1] The experiments reported here are focused on characterization of the molecular mechanism of thermal cyclopropane hydrogenation under catalytic conditions in the presence of gas-phase cyclopropane and hydrogen. The in situ soft X-ray methods used provide an interesting new perspective on the reactivity, stoichiometries, and bonding of adsorbed carbon containing species under reaction conditions.

In the early 1970s, Professor Somorjai pioneered the study of catalytic reactions on well-defined model surfaces by combining reactivity measurements with postreaction examination of the surface with vacuum-based techniques. As part of these efforts, Kahn, Peterson, and Somorjai characterized cyclopropane hydrogenolysis at atmospheric pressure on a stepped Pt(111) surface in 1974.[2] An apparatus for characterizing

the reactivity of well-defined single-crystal surfaces at atmospheric pressure was designed so that direct comparisons with supported platinum catalysts could be made. Direct comparisons of reactivities support the idea that similar reaction mechanisms dominate on supported and single-crystal Pt surfaces even at atmospheric pressures. Vacuum-based surface methods were used to examine the structure and composition of the single-crystal catalyst after reaction. This experimental strategy has resulted in substantial new understanding of structure/reactivity relationships on surfaces.[3] More recently, in situ methods for characterizing catalyst surfaces and reaction mechanisms under reaction conditions have become increasingly important and accessible. In situ methods allow direct examination of reactive species and surface reconstructions, which are not stable in the absence of reaction. Infrared sum frequency and scanning microscopy methods have played an important role in Professor Somorjai's recent efforts to provided new insights in to surface restructuring under reaction conditions and to establishing molecular mechanisms for catalytic reactions.[4] Progress in our understanding of complex catalytic materials and complex catalytic processes could be enhanced significantly by the development of new in situ methods for characterizing the structure of active sites and molecular processes during catalytic reactions. Fluorescence yield soft X-ray methods are emerging in situ methods that provide a new perspective regarding concentrations, stoichiometries, and bonding of adsorbed species under reaction conditions.[5] This paper reports on the use of these

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soft X-ray methods to characterize cyclopropane hydrogenation on the model Pt(111) surface over a range of temperatures and pressures. Soft X-ray methods promise to provide substantial new molecular mechanistic information regarding catalytic reactions on materials ranging from single crystals to complex optimized supported catalysts.

Catalytic hydrogenation of cyclopropane has been characterized on both supported and model platinum catalysts. Generally propane is the dominant product and activation energies in the 10−15 kcal/mol range are observed.[6] Although substantial effort has been directed toward understanding this model reaction, the role of hydrogen in bond breaking and the structure sensitivity of the reaction remains an active research topic. Recent studies in this group have focused on use of gas-phase hydrogen radicals to initiate reactions in weakly adsorbed cyclic hydrocarbons on Pt and Ni surfaces.[1] In adsorbed strained ring systems, reaction with gas-phase hydrogen radicals causes C−C bond activation resulting in the formation of adsorbed alkyl groups. Thus, gas-phase hydrogen radical induced cyclopropane ring opening provides a direct way to make adsorbed propyl. On the Pt(111) surface, adsorbed propyl reacts with coadsorbed hydrogen to form propane over the 170−220 K temperature range. The experiments reported here are focused on thermal cyclopropane hydrogenation under catalytic conditions in the presence of gas-phase cyclopropane and hydrogen. The results presented below suggest that propane formation under these catalytic conditions involves a propyl intermediate formed by hydrogenation of metallocycle intermediate formed by insertion of the surface into the strained cyclopropane ring.

Experimental Section

Cyclopropane hydrogenation was characterized using a combination of in situ soft X-ray techniques using the recently improved U7A beamline at the National Synchrotron Light Source (NSLS) located at Brookhaven National Laboratory. The U7A beamline was recently upgraded with a high throughput torodial-mirror/spherical grating monochromator described in detail elsewhere.[7] The U7A surface science endstation is equipped with a two-level experimental chamber dedicated to the investigation of surface reactions important in catalysis. The upper reaction/spectroscopy chamber (where these experiments were conducted) is equipped with a fluorescence yield detector optimized for carbon fluorescence.[8] The reaction/spectroscopy chamber is equipped with a 2000 Å Al window gate valve, which is approximately 20% transparent at 330 eV. The window is inserted to isolate the reaction/spectroscopy chamber from the upstream UHV Io chamber when "high pressure" in situ experiments are conducted. The upstream Io chamber contains a gold grid for Io measurements and 2 sets of adjustable beam defining apertures for reducing scattered light. The chamber is also equipped with an Au evaporator for depositing clean gold on the Io grid.

Both transient and spectroscopic studies were used to characterize cyclopropane hydrogenolysis on the Pt(111) surface. Temperature-programmed CIXAS (catalytic in-situ X-ray adsorption spectroscopy) experiments were used to characterize intermediates under a range of conditions. After the sample surface was cleaned and cooled to 90 K, the turbo pump was throttled heavily and cyclopropane flow was initiated at 2×10^{-8} Torr. Hydrogen flow was then initiated and the pressure adjusted to achieve the desired ratio. A 10% flow rate of gas was maintained during reaction to ensure reactant purity. The heating rate was 0.5 K/s during temperature-programmed experiments. Generally, during these experiments the total surface carbon concentration was monitored in the carbon continuum (330 eV). All temperature-programmed in situ experiments were performed with 450 μm/450 μm slits which results in a resolution of 1.2 eV. Repeated experiments indicate the thermal transitions are reproducible to 2 K. CO TP-FYNES desorption spectra were used to confirm the performance of this system and reproduce published results. Carbon coverages were determined by comparing the carbon continuum intensities observed during CIXAS experiments with intensity from a saturated monolayer of CO. The absolute carbon coverage of a saturated CO monolayer on this Pt(111) surface (9.6×10^{14} C atoms/cm^2) was used as a standard to calibrate the concentration scale for carbon containing species.[9] To expedite direct comparisons, all the surface concentration in this paper are reported in terms of C$_3$ molecules/cm^2. Fluorescence intensities at 330 eV from a CO saturated monolayer were checked regularly to ensure repeatability and consistency of experiments. Energy calibration was verified using the π^* adsorption of graphite on a graphite covered Io grid upstream of the reaction chamber.

In addition to characterizing the absolute carbon concentration on the surface, the average C−H stoichiometry of adsorbed species can be determined under reaction conditions using fluorescence yield measurements. The intensity of the C−H resonance is independent of molecular orientation at the "magic angle" of 55.4° so that C−H concentrations can be determined in this configuration. The relative ratio of the C−H (288 eV) to carbon continuum (330 eV) was used to estimate C−H stoichiometries based on a molecular cyclopropane standard (C$_3$H$_6$). The accuracy of this C−H stoichiometry method has been recently demonstrated during studies of propylene deep oxidation on the Pt(111) surface.[5] Fluorescence yield near edge spectroscopy (FYNES) above the carbon K edge was used to characterize adsorbed cyclopropane and the reaction intermediate under reaction conditions during these experiments. All FYNES spectra of adsorbed species were divided by a reference spectrum from a clean surface taken on the same ring fill to ensure consistency. Spectra were taken at two incident angles, 90° (normal) to the surface and 30° (glancing) to the surface, for each species. Spectra to be fit were standardized by setting the carbon pre-edge to zero and the carbon continuum to one to facilitate comparisons. To identify resonances, the carbon edge function was subtracted in the manner described by Stohr.[10] When possible, assignments were made based upon gas-phase ISEELS spectra and peaks were fitted to the spectra using Gaussian functions.

The Pt(111) crystal was mounted on Ta wire supports on the end of a 6 ft. liquid nitrogen cooled re-entrant manipulator. Temperature was measured with a 0.01 mm chromel−alumel (type K) thermocouple spot-welded to the back of the crystal and controlled with a RHK temperature controller. Initially, the crystal was cleaned by a combination of Ar$^+$ ion sputtering followed by annealing to 1000 K. During experimental runs, the sample was cleaned by annealing the crystal to 600 K in 0.002 Torr of oxygen for 1 min, followed by a 20 s anneal at 1000 K. Fluorescence at the carbon edge (330 eV) was used to verify cleanliness after oxidation.

Results

Cyclopropane adsorbs weakly and desorbs molecularly without significant reaction from the Pt(111) surface at 140 K as indicated in Figure 1. On the basis of the expected first-order desorption kinetics, a Redhead analysis yields an activation energy for desorption of 8.5 kcal/mol. No methane, ethane, propane, or higher hydrocarbon formation is observed during these TPRS experiments.[11] The small 140 K peaks at $m/e = 15, 28, 29$ are caused by fragmentation of cyclopropane in the

Catalytic Cyclopropane Hydrogenation on Platinum(111)

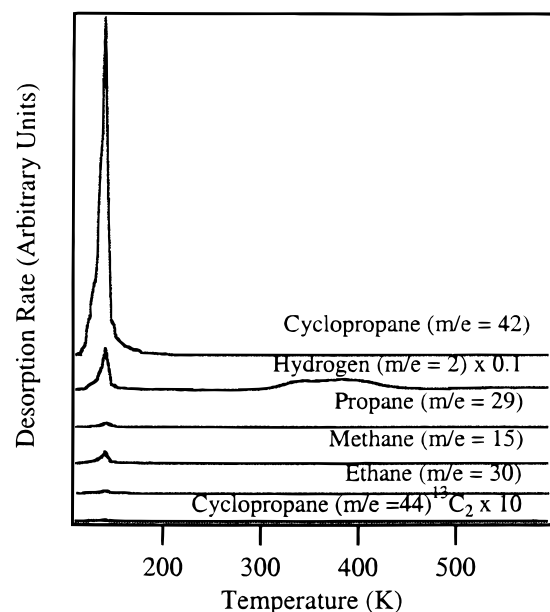*J. Phys. Chem. B, Vol. 104, No. 14, 2000* **3339**

Figure 1. Temperature-programmed desorption spectra for a saturated monolayer of cyclopropane on the Pt(111) surface. Note that the cyclopropane desorbs at 140 K.

mass spectrometer. The small 140 K peak in the propane parent ($m/e = 44$) trace results from the natural abundance of double ^{13}C cyclopropane. The hydrogen ($m/e = 2$) TPR spectrum has a small peak at 350 K resulting from dehydrogenation on defect sites.

Spectra for a saturated monolayer of cyclopropane adsorbed on the Pt(111) surface at 100 K are shown in Figure 2 at normal and glancing incidence. Published spectra of gas-phase cyclopropane and related C$_3$ molecules were used as the basis for spectroscopic assignments.[10,12] In the normal spectrum (upper panel), the resonance at 285 eV is associated with an adsorbed ring π transition, 288 eV is associated with a C−H transition, 293 eV with a C−C transition, and 299 eV with a second C−C transition. Similar resonance energies are observed in the glancing spectrum (lower panel). The intensity of the small ring π transition increases at glancing incidence, while all the other intensities decrease at glancing incidence. The resonance at 310 K which appears in both spectra is a molecular multiple scattering peak, which has been observed in C$_3$ multilayer NEXAFS spectra.[13] Each spectrum was fit using the standard procedure outlined in the Experimental Section. The profile of the carbon edge is indicated by a dashed line. Cyclopropane's orientation on the surface can be estimated using angular variation of the ring π, C−H, and the C−C resonance intensities. Because of minimum overlap with the carbon continuum intensities of the ring π and CH provide the best measure of orientation. Since the ring π lies in the plane of the cyclopropane, the orientation of the ring π resonance matches the orientation of the cyclopropane molecule. Using a polarization factor of 0.9, we estimated that the cyclopropane ring is tilted 30° up from the surface plane based on the π ring resonance. An estimate based on the intensities of the C−H resonance confirm the ring is tilted up from the surface by about 25° plane. This tilted adsorbed configuration is similar to previously proposed adsorption geometries for cyclopropane on metal surfaces.[14] The intensity in the carbon continuum region (330 eV) was used to determine that a saturated cyclopropane monolayer at 100 K contains 4.4×10^{14} cyclopropane molecules per cm^2 based on standards indicated in the Experimental Section.
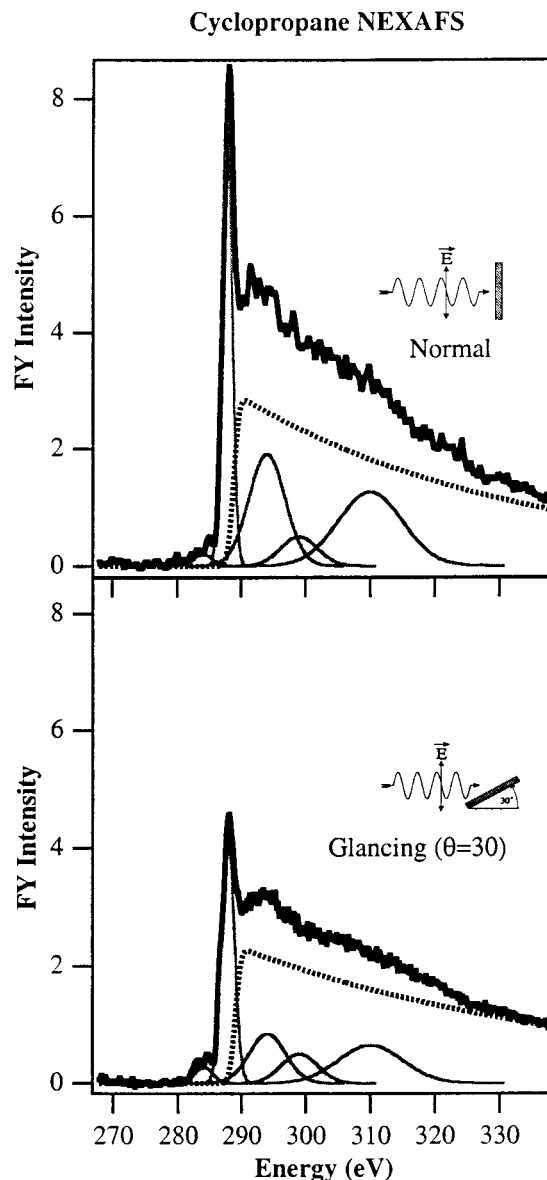
Cyclopropane NEXAFS

Figure 2. Normalized FYNES spectra of a saturated monolayer of cyclopropane at 100 K. The upper spectrum is at normal incidence while the lower spectrum was taken at 30° incidence. On the basis of the angular dependence of the ring π and the C−H resonance the cyclopropane ring is tilted up from the surface by approximately 30°.

Batch reactor studies indicate that 2×10^{-8} Torr of cyclopropane and 0.002 Torr of hydrogen react to form propane on the Pt(111) surface at 350 K (Figure 3). No significant propane formation was detected after exposure to the Pt(111) surface at 120 K as indicated by the negligible propane ($m/e = 29$) and residual cyclopropane ($m/e = 42$) concentrations shown in the left panel of Figure 3. The small signal detected at $m/e = 29$ in the blank correlates with fragmentation of cyclopropane in the mass spectrometer.[15] Substantial propane formation and depletion of the cyclopropane reactant was observed after exposure to the Pt(111) surface at 350 K as shown in the right panel of Figure 3. No methane and ethane were detected during these experiments. These results are consistent with previous catalytic studies for cyclopropane hydrogenation where the maximum rate of propane formation occurred between 300 and 350 K.[16] On the basis of the observation of only a propane product, the dominant surface species appears to remain a C$_3$ species up to 350 K.

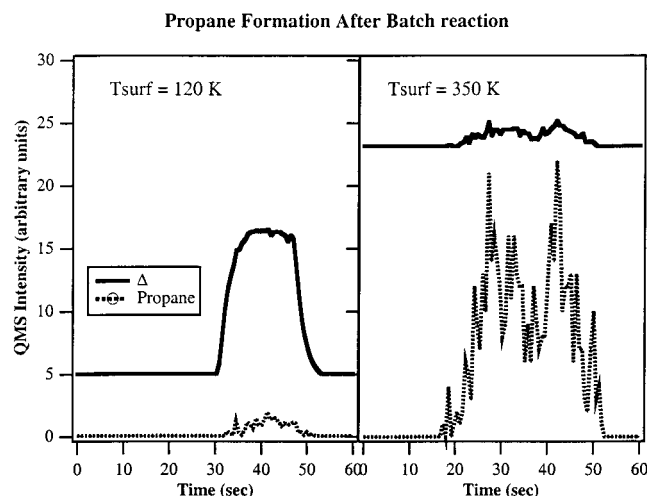**Propane Formation After Batch reaction**

Figure 3. Cyclopropane hydrogenation at 350 K is indicated by the appearance of the product propane and the depletion of cyclopropane in the right panel. No hydrogenation is observed in the blank experiment shown in the left panel. During reaction the atmosphere was composed of 2×10^{-8} Torr of cyclopropane and 0.002 Torr of hydrogen.
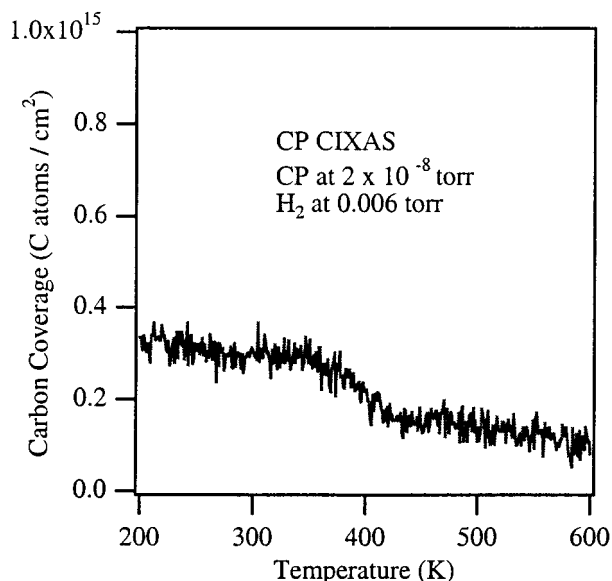

Figure 4. Carbon concentration (330 eV) as a function of temperature in 2×10^{-8} Torr of cyclopropane and 0.002 Torr of hydrogen. The concentration of adsorbed carbonaceous species falls from 3.2×10^{14} C_3 molecules/cm^2 at 200 K to 1.0×10^{14} C_3 molecules/cm^2 at 600 K. At the 350 K reaction temperature, the carbon concentration is 2.9×10^{14} C_3 molecules/cm^2.

Fluorescence yield measurements in the carbon continuum (330 eV) were used to characterize the carbon-containing surface species that are stable up to 400 K under reaction conditions (Figure 4). The thermal stability of these species clearly indicates strong bonding with the surface which indicates that new cyclopropane derived species are present on the surface. As mentioned previously, all the surface concentrations in this paper are reported in terms of C_3 molecules/cm^2. With a mixture of cyclopropane and hydrogen in the gas-phase, the carbon concentration decreases gradually from 3.2×10^{14} C_3 molecules/cm^2, at 200 K, to 2.9×10^{14} C_3 molecules/cm^2, at 350 K. As the temperature increases from 350 to 420 K, the surface carbon level drops rapidly to 1.2×10^{14} C_3 molecules/cm^2. Under these temperature-programmed reaction conditions, 60% of the adsorbed carbon-containing species can be removed in the temperature range where rapid cyclopropane hydrogenation is expected. After this rapid drop, the carbon level gradually
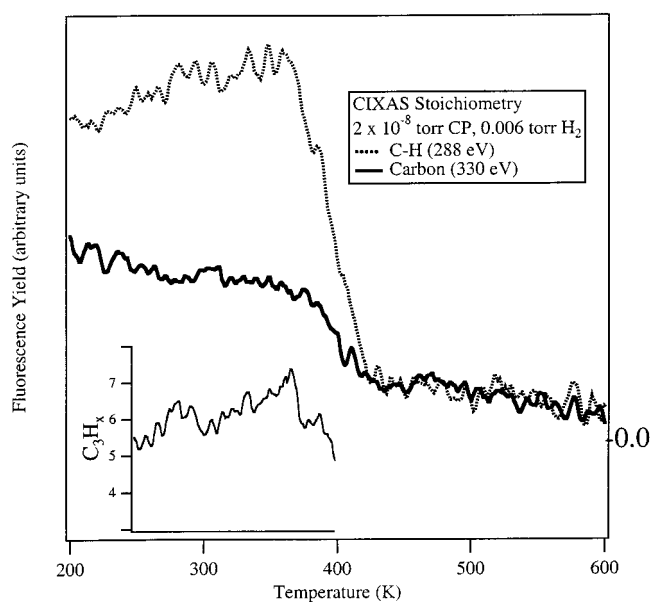

Figure 5. Carbon continuum fluorescence (solid line) and C—H resonant intensity (dashed line) at the magic angle. The temperature was ramped linearly at 0.5 K/s in 2×10^{-8} Torr of cyclopropane and 0.006 Torr of hydrogen. The calibrated stoichiometric ratio in the insert indicates that the average stoichiometry is C_3H_6 at 320 K and C_3H_7 at 350 K.

decreases from 1.2×10^{14} C_3 molecules/cm^2 at 420 K to 1.0×10^{14} C_3 molecules/cm^2 at 600 K.

To characterize the stoichiometry of the adsorbed carbon-containing species under reaction conditions, stoichiometric CIXAS experiments were performed (Figure 5). Surface C—H concentrations were estimated by measuring the intensity of the C—H resonance at the "magic angle" of 55.4° where the intensity is independent of molecular orientation.[10] The intensity of the CH resonance (288 eV) as a function of temperature is indicated by the dashed line, while the intensity in the carbon continuum at 330 eV is indicated by the solid line (Figure 5). Note that with increasing the temperature to 380 K the C—H intensity increases while the carbon concentration decreases. These changes indicate an increase in the C—H stoichiometry with increasing temperature. The stoichiometric ratio of C—H intensity relative to the total carbon intensity (inset Figure 5) was calibrated based on a molecular cyclopropane standard. The average C—H stoichiometry increases from near C_3H_6 at 320 K to near C_3H_7 at 350 K. A series of temperature-programmed isotope exchange experiments (not shown) was performed on the Pt(111) surface. Complete exchange was observed for all dehydrogenated species, while no exchange was observed for the molecular cyclopropane.

The activation energy for hydrogenation of the C_3H_7 surface species in the 300—450 K temperature range is similar to known activation energy for catalytic cyclopropane hydrogenation over platinum. A series of isothermal hydrogenation experiments were performed in the 350—380 K temperature range to determine activation energies (Figure 6). During these isothermal experiments the surface species were formed by increasing the temperature at 0.5 K/s with 2×10^{-8} Torr of cyclopropane and 0.002 Torr of hydrogen in the gas phase. At reaction temperature, the cyclopropane was removed from the gas phase and the decrease in surface carbon concentration (330 eV) was measured as a function of time. Rate constants for carbon removal were determined using first-order kinetics. An Arrhenius plot for hydrogen removal of carbonaceous surface species is shown in Figure 6. The activation energy for removal
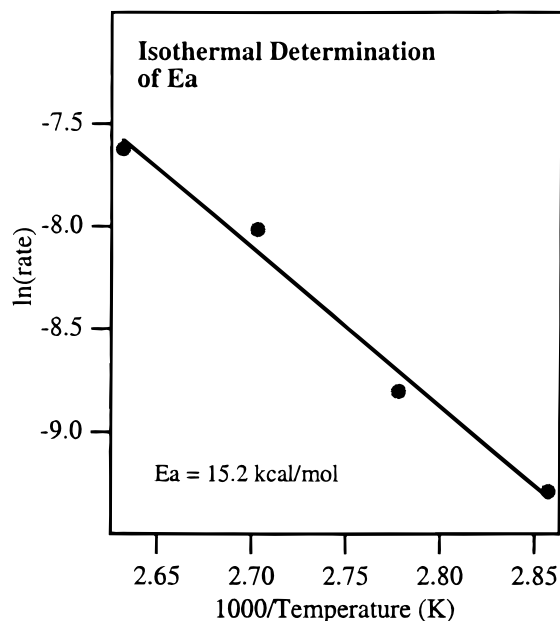
Figure 6. Isothermal kinetic measurements over the 350 to 380 K temperature range indicate that hydrogenation of the surface intermediate has an activation energy of 15.2 kcal/mol.

of these C_3H_7 species is 15.2 kcal/mol, which agrees with 12 kcal/mol found for cyclopropane hydrogenation over platinum surfaces.[2]

NEXAFS spectroscopy was used to characterize the structure of the C_3H_6 species formed at 320 K. The sample was ramped at 0.5 K/s to 320 K in 2×10^{-8} Torr of cyclopropane and 0.002 Torr of hydrogen and held at 320 K during spectral acquisition. NEXAFS spectra at glancing and normal incidence are shown in Figure 7. A temperature of 320 K was chosen because the concentration of this C_3H_6 species remained sufficiently stable to ensure directly comparable spectra could be obtained at normal and glancing incidence. The peak at 288 eV is the C–H resonance, and the peak at 296 eV is a C–C resonance. The 303 eV resonance is not observed for adsorbed cyclopropane and is consistent with energies expected for a C–Pt resonance. Note the absence of the ring π resonance in the intermediate at 285 eV which was observed for molecular cyclopropane. The resonance at 310 eV is a C_3 multiple scattering resonance. Examination of general spectral shape and relative peak intensities clearly shows that this intermediate cannot be cyclopropane. The C–H resonance shows a large angular dependence, with the normal incidence intensity larger than the intensity at glancing incidence. Analysis of the C–H angular dependence indicates that on average the C–H bonds are nearly parallel to the surface. In contrast, the C–C resonances are much larger at glancing incidence than at normal incidence. This indicates that the C–C bonds are upright relative to the surface. The decreased intensity of the C–C resonances in the intermediate is consistent with ring opening which should result in a decrease in the number of C–C bonds. These observations are consistent with formation of a C_3H_6 platinacylobutane intermediate adsorbed in a upright configuration on the surface.

Discussion

These in situ catalytic studies are focused on catalytic cyclopropane hydrogenation on the Pt(111) surface. At low temperature, cyclopropane is weakly adsorbed and tilted slightly up from the surface. The desorption energy for molecular cyclopropane (8.5 kcal/mol) is substantially smaller than the activation energy for hydrogenation (15 kcal/mol), so adsorbed
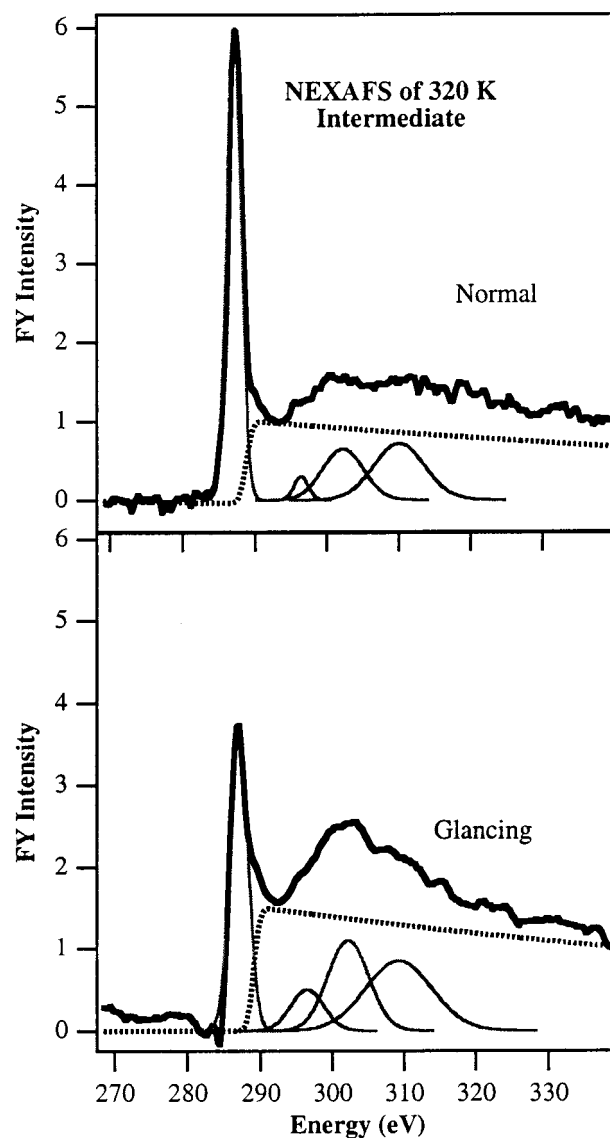

Figure 7. Normalized FYNES spectra of the cyclopropane derived intermediate species at 320 K in 2×10^{-8} Torr of cyclopropane and 0.002 Torr of hydrogen. The upper spectrum is at normal incidence while the lower spectrum was taken at 30° incidence. On the basis of the angular dependence of the C–C and C–H resonances, the platinacyclobutane intermediate is adsorbed in an upright configuration.

cyclopropane desorbs before reacting with hydrogen in agreement with previous studies.

In the presence of both cyclopropane and hydrogen gas, the Pt(111) surface is an effective hydrogenation catalysts (Figure 3). The observation that propane is the only product observed indicates that no multiple C–C bond breaking occurs under these condition on the Pt(111) surface even in large excesses of hydrogen. Since no multiple C–C bond breaking is observed in the gas-phase products, the dominant cyclopropane derived surface species appear to remain C_3 species through this temperature range. Direct support for a C_3 species is also provided by the intensity of the C–C resonances in the 320 K intermediate (Figure 7). Several kinetic measurements support the proposal that these cyclopropane derived C_3 species are involved directly in propane formation. In situ isothermal reactivity studies in hydrogen in the 350–380 K temperature range indicate that the cyclopropane derived species is removed from the surface with a thermal activation energy of 15.2 kcal/

3342 *J. Phys. Chem. B, Vol. 104, No. 14, 2000*

Capitano et al.

mol (Figure 6). This activation energy agrees with reported activation energies for catalytic cyclopropane hydrogenation over platinum catalysts. During temperature-programmed experiments, the concentration of these species decreases rapidly between 350 and 400 K (Figure 4). Reactivity measurements demonstrate that propane formation occurs at 350 K in this same temperature range under the same conditions on this Pt(111) surface (Figure 3). Taken together, the observation of catalytic propane formation at 350 K, the similarity in temperature ranges for cyclopropane derived surface species removal and propane formation, and the measured activation energies for cyclopropane derived surface species removal support the proposal that this surface species is an intermediate for propane formation on the Pt(111) surface.

The stoichiometry and bonding of the C_3 intermediate which forms at 320 K has been characterized under reaction condition using soft X-ray methods. Calibrated C−H intensity ratios determined during temperature-programmed experiments indicate that a C_3H_6 species is dominant at 320 K. The bonding of this C_3H_6 intermediate was characterized using soft X-ray spectroscopy under reaction conditions at 320 K (Figure 7). The general spectroscopic profile clearly indicates this species is not cyclopropane despite the C_3H_6 stoichiometry. To identify this intermediate, NEXAFS spectra of propane, 1-propyl, 2-propyl, propene, propylidyne, and propyne were preformed.[17] However, the spectra of none of these species corresponded to the intermediate, indicating that another C_3 species must be responsible for cyclopropane hydrogenation. The upright carbon framework and parallel C−H bond suggest that the C_3H_6 species is an adsorbed C_3 metallocycle intermediate adsorbed in an upright configuration on the surface. At elevated temperature, the Pt surface appears to insert into on the strained C−C bond in cyclopropane to form an intermediate. All the features in the soft X-ray spectrum are consistent with a platinacylobutane intermediate adsorbed in an upright orientation. This strongly bound C_3H_6 intermediate is stable at 320 K in large excesses of hydrogen. Deuterium exchange experiments reported here for cyclopropane on the Pt(111) surface are consistent with this intermediate. Similar intermediates have been previously proposed for cyclopropane hydrogenation on supported Pt catalysts based on isotope incorporation studies.[18,19]

With increasing temperature, this platinacyclobutane intermediate is hydrogenated to form propane in the 350 to 380 K temperature range. When the temperature is increased from 320 to 350 K, the average C−H stoichiometry increases from C_3H_6 to C_3H_7. This increased hydrogenation suggests that at reaction temperature the platinacyclobutane intermediate is hydrogenated to form a propyl species during propane formation. Unfortunately, at this time reliable spectra could not be obtained at 350 K because of experimental difficulties caused by the sensitivity of surface coverages to precise control of reactant pressures over the extended time period required for spectral acquisition with the current facilities. However, these stoichiometric results clearly suggest that the metallocycle intermediate is sequentially hydrogenated during the propane formation process. Previous studies regarding propyl hydrogenation on the Pt(111) surface indicate that once propyl is formed, hydrogenation would be rapid in this temperature range. Mechanistic studies involving hydrogenation of alkyl substituted cyclopropane over supported Pt catalysts have also suggested that propane formation involves a metallocyclobutane intermediate.[18,19]

The picture which emerges regarding catalytic cyclopropane hydrogenation is quite interesting. A substantial concentration of adsorbed metallocycle intermediate is stable on the Pt(111) surface at elevated temperatures under reaction conditions. Hydrogenation of this stable intermediate appears to be responsible for catalytic propane formation in the 350 K temperature range where substantial coverages of molecular cyclopropane cannot be maintained on the surface. The addition of hydrogen to the metallocycle intermediate appears to be sequential with a transient propyl species formed during the propane formation process.

Summary

In situ soft X-ray techniques have provided a new perspective regarding the mechanism of cyclopropane hydrogenation on the Pt(111) surface. By combining in situ spectroscopic and transient measurements, the processes responsible for catalytic cyclopropane have been probed at the molecular level. Advances in both soft X-ray sources and detectors promise to rapidly improve our ability to characterize catalytic reactions over a range of increasing complex catalytic materials.

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