Methane Dissociative Adsorption on the Pt(111) Surface over the 300−500 K Temperature and 1−10 Torr Pressure Ranges

Anderson L. Marsh, Kevin A. Becraft, and Gabor A. Somorjai*

Department of Chemistry, University of California, Berkeley and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

The dissociative adsorption of methane on the Pt(111) surface has been investigated and characterized over the 1−10 Torr pressure and 300−500 K temperature ranges using sum frequency generation (SFG) vibrational spectroscopy and Auger electron spectroscopy (AES). At a reaction temperature of 300 K and a pressure of 1 Torr, C−H bond dissociation occurs in methane on the Pt(111) surface to produce adsorbed methyl (CH_3) groups, carbon, and hydrogen. SFG results suggest that C−C coupling occurs at higher reaction temperatures and pressures. At 400 K, methyl groups react with adsorbed C to form ethylidyne (C_2H_3), which dehydrogenates at 500 K to form ethynyl (C_2H) and methylidyne (CH) species, as shown by SFG. By 600 K, all of the ethylidyne has reacted to form the dissociation products ethynyl and methylidyne. Calculated C−H bond dissociation probabilities for methane, determined by carbon deposition measured by AES, are in the 10^{-8} range and increase with increasing reaction temperature. A mechanism has been developed and is compared with conclusions from other experimental and theoretical studies using single crystals.

Introduction

The activation of carbon−hydrogen bonds in methane for conversion to hydrogen or to other hydrocarbons is one of the fundamental problems of catalytic surface chemistry.[1−2] Classical surface science studies of C−H dissociation in methane on Pt(111) under ultrahigh vacuum (UHV) conditions have been limited because of the low (<70 K) desorption temperature of the methane monolayer from this single-crystal surface.[3−5] Because of this limitation, the dissociative adsorption of methane on Pt(111), at temperatures above the monolayer desorption temperature, has been investigated previously using mainly molecular beam methods.[6−12] In some instances, various surface-sensitive techniques have been used to identify adsorbed surface intermediates.[8,11] On Pt(111), methyl groups were identified as products from the reaction of a hyperthermal molecular beam of methane at a surface temperature of 150 K using reflection absorption infrared spectroscopy (RAIRS).[8] For a surface temperature of 400 K, ethylidyne was proposed to form, on the basis of changes in the vibrational spectrum for the adsorbed surface species. In an in-situ vibrationally resolved X-ray photoelectron spectroscopy (XPS) study, photoemission peaks corresponding to methyl groups were observed at low temperatures.[11] Above 260 K, methylidyne peaks were seen in the spectra, while above 500 K only peaks corresponding to adsorbed C were detected.

Methane C−H bond activation has been investigated on other metal single-crystal surfaces as well.[13−14] On the Ni(111) surface, methyl groups were formed from reaction of molecular beams at a surface temperature of 475 K, as indicated by high-resolution electron energy loss spectroscopy (HREELS).[13] Adsorbed surface species formed after high-pressure (5 Torr) methane reactions on the Ru(0001) and Ru(1120) surfaces were also characterized by HREELS experiments performed after evacuation of the gas phase to UHV conditions.[14] Peaks for methylidyne and vinylidene groups were observed over the 400−700 K temperature range. The results of these investigations clearly show a wide range of reactions for methane on single-crystal surfaces; however, the spectroscopic experiments described above were performed under UHV conditions.

Sum frequency generation (SFG) vibrational spectroscopy is a powerful technique for in-situ investigation of catalytic reactions on smooth surfaces such as those of a single crystal.[15−16] In this work, SFG vibrational spectroscopy has been used in combination with Auger electron spectroscopy (AES) to characterize the formation of species from methane dissociative adsorption on the Pt(111) surface over the 300−500 K temperature and 1−10 Torr pressure ranges. For a reaction temperature of 300 K and a methane pressure of 1 Torr, adsorbed methyl (CH_3) groups have been identified on the Pt(111) surface using SFG. The dissociation probability, which is in the 10^{-8} range, increases with increasing reaction temperature, as determined from AES experiments measuring an increased amount of adsorbed C on the surface for higher reaction temperatures. C−C coupling occurs when methyl groups react with adsorbed C to form ethylidyne (C_2H_3) with increasing reaction temperatures and pressures. These surface intermediates further dehydrogenate with increasing reaction temperature to form ethynyl (C_2H) and methylidyne (CH) species. Taken together, these findings provide further insight into the intermediates and mechanisms during reactions of methane on the Pt(111) surface.

Experimental Section

These experiments were conducted in a stainless steel UHV chamber with a working base pressure of $<2 \times 10^{-10}$ Torr.[17] This pressure is achieved through a combination of turbo-molecular, ion, and Ti sublimation pumping. The chamber is equipped with a Stanford Research Systems mass spectrometer for residual gas analysis, as well as Omicron SPECTALEED

* Author to whom correspondence should be addressed. Phone: (510) 642-4053; fax: (510) 643-9668; e-mail: somorjai@socrates.berkeley.edu.

optics for Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). A highly polished Pt(111) single crystal was mounted by spot-welding to Ta wires on a sample manipulator capable of $x-y-z$ motion and 360 degree rotation. The crystal could be cooled to 150 K by flowing liquid nitrogen and be resistively heated to temperatures as high as 1150 K. The initial cleaning procedure consisted of repeated cycles of Ar^+ sputtering followed by heating in 5×10^{-7} Torr of oxygen at 700 K and then subsequent annealing in UHV at 1100 K. These cycles were repeated until surface impurities were undetectable by AES and a well-ordered (111) surface was produced as verified by a sharp (1×1) LEED pattern.

For the SFG experiments, a 20 Hz Continuum Nd:YAG laser was used to produce 20 ps pulses at a fundamental frequency of 1064 nm. The laser output was directed into a LaserVision OPG/OPA system and was split to produce a 532-nm visible beam and a tunable infrared beam. The beams were spatially and temporally overlapped on the Pt(111) surface and the resultant SFG signal was collected and focused into a mono-chromator and then was measured using a photomultiplier tube interfaced with a gated integrator and personal computer. Both the incident visible and infrared beams were p-polarized, which results in p-polarized sum frequency output. SFG spectra were normalized by the incident infrared energy. Control experiments indicate no significant gas-phase absorption by the infrared beam occurs over the pressure range investigated. Spectra were curve fit using a procedure reported previously[18-19] to a form of the equation

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

where $\chi_{NR}^{(2)}$ is the nonresonant nonlinear susceptibility, $e^{i\phi_{NR}}$ 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.

The high-pressure reaction experiments were conducted in the following manner. First, the crystal was cleaned by Ar^+ sputtering followed by heating in 5×10^{-7} Torr of oxygen at 700 K. After thermally annealing in UHV, the crystal was cooled to <250 K, and then the upper part of the chamber was isolated from the UHV pumping by a gate valve. Next, research grade methane (Airgas, 99.999%), which was further purified by an Alltech ALL-Pure hydrocarbon trap, was introduced into the chamber at the desired reaction pressure through a right angle valve. The crystal was then heated to the selected reaction temperature and was held for 60 s before cooling to <200 K. In the case of AES experiments, the chamber was evacuated and returned to UHV conditions before recording a spectrum. For SFG experiments, the gas remained in the chamber during the course of recording a spectrum. Low temperatures were maintained during acquisition of SFG spectra to limit further dehydrogenation of the methane-derived reaction species and to increase signal-to-noise levels by decreasing surface diffusion and increasing surface ordering.

Results and Discussion

The probabilities for dissociative adsorption methane on the Pt(111) surface have been calculated on the basis of carbon deposition measured using Auger electron spectroscopy. The results of AES experiments at selected reaction temperatures
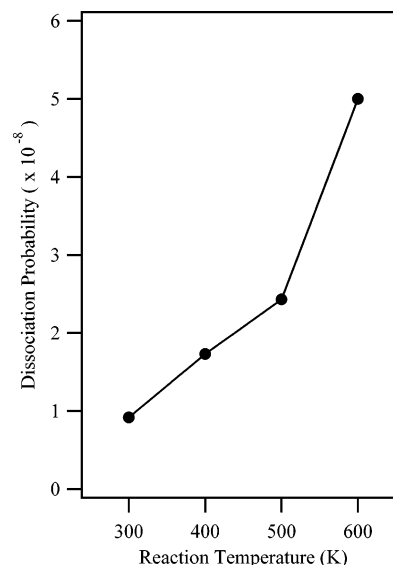

Figure 1. Methane C−H dissociation probabilities derived from carbon coverages measured by AES for selected reaction temperatures.

are displayed in Figure 1. As observed in this work, methane reacts with the Pt(111) surface to produce adsorbed carbon species at temperatures as low as 300 K. The presence of adsorbed C is identified by the appearance of a peak at 272 eV in the Auger spectrum. Dissociation probabilities in Figure 1 were calculated by first converting the ratio of the peak-to-peak intensities of the C 272 eV transition to the Pt 237 eV transition to absolute carbon coverage in molecules/cm^2 using a method published previously.[20] This value was then divided by the flux of methane molecules incident to the Pt(111) surface over a period of 60 s. (For a methane pressure of 1 Torr, the flux is 5.0×10^{20} molecules/cm^2/s.) As seen in the figure, the dissociation probabilities are in the 10^{-8} range and increase with increasing temperature. This finding is consistent with those from molecular beam kinetic experiments[6,9] and a model based on microcanonical unimolecular rate theory,[21] where the initial sticking probability was found to increase with increasing surface temperature. The order of magnitude of these calculated dissociation probabilities is similar to those measured for the dissociative adsorption of 1 Torr of methane at 500 K on the Ni(111) surface.[22] The low probability of dissociative adsorption clearly suggests that high pressures are required for this reaction to occur under these experimental conditions.

SFG spectra indicating the molecular structures of the various methane-derived intermediates adsorbed on the Pt(111) surface after reaction at selected temperatures are shown in Figure 2. For a reaction temperature of 300 K, a single vibrational peak is present at 2880 cm^{-1} in the spectrum, indicating the presence of CH_3 groups on the surface. This peak is assigned to the symmetric C−H methyl stretch. This assignment is consistent with those from previous vibrational spectroscopic studies of methyl groups deposited on the Pt(111) surface by various methods.[8,23-26] On the basis of the position of this vibrational peak and the absence of a peak at 2950 cm^{-1} because of the asymmetric C−H methyl stretch, the methyl groups are adsorbed on atop sites with C_{3v} symmetry.[24,25] Increasing the reaction temperature leads to a change in the SFG spectrum, as seen in the figure. When the reaction temperature was increased to 400 K, the peak increased in intensity and the line width narrowed; however, the peak position remained at 2880 cm^{-1}. This peak is assigned to adsorbed ethylidyne, on the basis of previous SFG studies.[27] The line width of this peak, as determined from curve fitting, is ~10 cm^{-1}, whereas the line width of the peak in the

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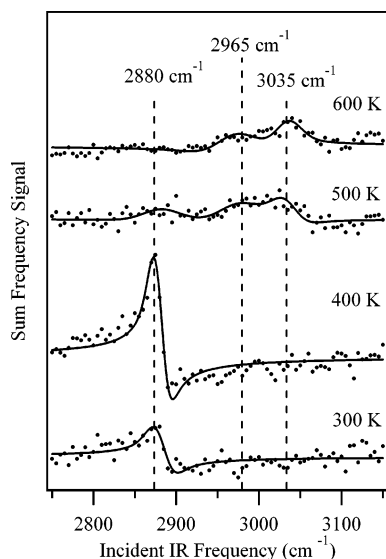*J. Phys. Chem. B, Vol. 109, No. 28, 2005* **13621**

Figure 2. SFG spectra recorded after reaction of 1 Torr of methane for 60 s with the Pt(111) surface at selected reaction temperatures. Markers represent the experimental data, and solid lines represent the curve fits.

Figure 3. SFG spectra recorded after reaction of selected pressures of methane for 60 s with the Pt(111) surface at 300 K. Markers represent the experimental data, and solid lines represent the curve fits.

300 K spectrum is $\sim$15 cm^{-1}. The smaller line width is consistent with that for an ethylidyne species absorbed on Pt(111). The second carbon atom present in ethylidyne increases the distance of the methyl group from the metal surface, therefore decreasing the interaction of this vibrational mode with the surface electrons and resulting in the decrease in line width. For high coverages of methyl groups adsorbed on the Pt(111) surface, C−C coupling has been shown to occur, on the basis of infrared vibrational spectra, to produce ethylidyne.[8,23] RAIRS experimental evidence suggests the line width of the C−H symmetric methyl stretch is decreased for adsorbed ethylidyne compared to that for adsorbed methyl.[23]

The peak at 2880 cm^{-1} is considerably decreased in intensity in the spectrum corresponding to a reaction temperature of 500 K, and two new peaks appear in the vibrational spectrum: one at 2965 cm^{-1} and the other at 3035 cm^{-1}. These peaks are consistent with the presence of methylidyne (CH) and ethynyl (CCH) species, as reported previously for ethylidyne decomposition on Pt(111) using RAIRS[28] and carbon hydrogenation using HREELS.[29] On the basis of these studies, the 2965 cm^{-1} peak is therefore assigned to methylidyne and the 3035 cm^{-1} peak is assigned to ethynyl. The presence of these two peaks and the decrease in the intensity of the 2880 cm^{-1} peak clearly indicates the decomposition of adsorbed ethylidyne. As seen in the figure, both of these peaks are present in the SFG spectrum corresponding to a reaction temperature of 600 K, indicating further ethylidyne decomposition.

SFG spectra comparing the various methane-derived intermediates adsorbed on the Pt(111) surface at selected reaction pressures are shown in Figure 3. As mentioned in the above paragraph, for a reaction pressure of 1 Torr and temperature of 300 K, a vibrational peak arising from the methyl symmetric stretch is present at 2880 cm^{-1} in the SFG spectrum, indicating the presence of CH$_3$ groups on the surface. For a reaction pressure of 10 Torr, the peak increases in intensity significantly and the line width narrows, as seen in the corresponding spectrum in the figure. This peak is assigned to ethylidyne on the basis of similar arguments presented earlier. No other peaks are present in this spectrum, as observed with the spectrum for a reaction temperature of 400 K. The findings will be further
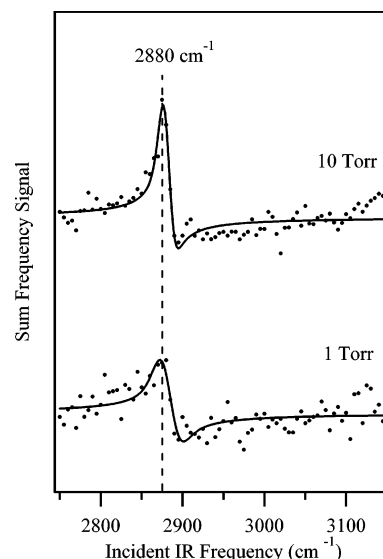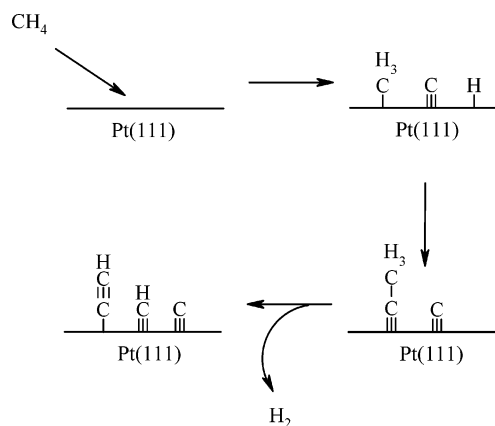

Figure 4. Mechanism and intermediates for methane dissociative adsorption and reaction of methane-derived species on the Pt(111) surface over the 300−500 K temperature and 1−10 Torr pressure ranges.

discussed below, and a mechanism summarizing the conclusions is presented.

A mechanism for methane dissociative adsorption and subsequent reaction on the Pt(111) surface has been developed and is shown in Figure 4. At 1 Torr and 300 K, C−H bond dissociation in methane occurs on the Pt(111) surface to produce adsorbed methyl groups, carbon, and hydrogen. Evidence for CH$_3$ intermediates on other platinum catalyst surfaces exists from isotopic exchange experiments.[30−31] CH$_3$D was produced during exposure of methane and deuterium to platinum thin films[30] and supported platinum catalysts.[31] Recent density functional theory (DFT) calculations indicate that the reaction of gas-phase methane with the Pt(111) surface to produce adsorbed methyl (CH$_3$) and hydrogen atoms (H) is exothermic, while the production of methylene (CH$_2$) or methylidyne (CH) from methyl is endothermic.[32] It is likely that methane initially dehydrogenates completely to adsorbed C and H, which then stabilize adsorbed methyl groups by inhibiting further C−H dissociation. Hydrogen desorbs from this surface for temperatures above 300 K[33] but under these reaction conditions may likely remain on the surface at 300 K. At present, we are unable to determine if initial C−H dissociation occurs at a small number of defect sites on the Pt(111) crystal. The exothermic nature of

the reaction to produce adsorbed CH_3 and H species would be consistent with the low (300 K) reaction temperature required for C−H activation. Nonetheless, the calculated dissociation probabilities suggest that high pressures are required for the reaction to proceed under these experimental conditions.

For higher reaction temperatures and pressures, concomitant dehydrogenation and C−C coupling take place to produce an adsorbed ethylidyne intermediate. At this higher temperature, adsorbed methyl groups would likely be more mobile on the surface and may react with adsorbed C to produce ethylidyne. DFT calculations have also shown this reaction to be exothermic on Pt(111).[32] C−C coupling has been observed during the hydrogenation of methane-derived adsorbates on a platinum catalyst to produce higher hydrocarbons.[34] In that study, the platinum catalyst was first exposed to methane gas and then was exposed to hydrogen gas. During the exposure to hydrogen gas, ethane was seen as a product. The authors suggest that C−C coupling takes place between dehydrogenated CH_x species on the surface during the chemisorption of methane.[35] In the work presented here, the formation of ethylidyne for a reaction temperature of 400 K would be commensurate with the detection of ethylidyne decomposition products at higher reaction temperatures.[28] SFG spectra indicate that adsorbed methane-derived ethynyl and methylidyne species are present on the surface for reaction temperatures of 500 and 600 K. These intermediates are most likely produced through the decomposition of ethylidyne, which is formed first.

Conclusions

In summary, C−H activation in methane has been characterized on the Pt(111) surface using sum frequency generation (SFG) vibrational spectroscopy and Auger electron spectroscopy (AES) over the 300−500 K temperature range for 1−10 Torr methane pressures. C−H dissociation occurs in methane on Pt(111) at 300 K and 1 Torr to produce adsorbed methyl (CH_3) groups and C. AES results indicate that the dissociation probabilities, which are in the 10^{-8} range, increase with increasing reaction temperature. C−C coupling occurs at higher reaction temperatures and pressures, as shown by changes in the SFG spectra. Ethylidyne (C_2H_3) forms from the reaction of methyl groups and adsorbed C and then subsequently dehydrogenates to form ethynyl (C_2H) and methylidyne (CH) species, as shown by SFG, with increasing reaction temperature. Future work will discuss the effects of coadsorbed H and C atoms and the role of defect sites in C−H activation on stepped platinum single surfaces.

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