

## Surface Science Letters

# Carbon–carbon coupling of methyl groups on Pt(111)

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Although methyl radicals are widely postulated to be important intermediates in many catalytic processes involving hydrocarbon species, relatively little is known about their reaction kinetics on metal surfaces. In order to more fully understand the surface chemistry of methyl groups we have developed a source of gas-phase methyl radicals based on the pyrolysis of azomethane. The surface chemistry of methyl groups adsorbed on Pt(111) has been studied using TPD and reflection-absorption infrared spectroscopy (RAIRS). Methyl radicals can be dosed directly onto the surface at 150 K and are bound in a  $C_{3v}$  geometry. Methyl groups become thermally activated above 230 K, reacting to produce a hydrogenation product (methane) and various dehydrogenation products. The nature of these dehydrogenation products depends upon the initial methyl coverage. At low coverages  $CH_x$  ( $x < 3$ ) species are predominant while at higher methyl coverages there is evidence of carbon–carbon coupling reactions to produce higher order hydrocarbons one of which has been identified as ethylidyne ( $C-CH_3$ ). Ethylidyne is also observed as a reaction product on Pt(111), at 150 K, for large methyl radical exposures.

## 1. Introduction

Surface alkyl groups have been proposed as intermediates in such diverse processes as catalytic hydrocarbon conversion and chemical vapor deposition. In recent years the surface chemistry of the simplest alkyl group, methyl, has been the subject of several surface science studies [1–5]. The objective of much of this work has been to map out in detail the pathways and kinetics of reactions involving methyl groups on the surface.

Methyl groups have been generated on transition metal surfaces, at low temperatures, through thermal or photochemical dissociation of methyl halides [1–5]. In general the surface reactions of adsorbed methyl groups are found to depend on

both the nature of the underlying substrate as well as the initial methyl coverage. For example, on Ni(111) methyl is found to undergo dehydrogenative coupling to form benzene with surface methylidyne (CH) and acetylene ( $C_2H_2$ ) as intermediates [6]. The chemistry of methyl on Cu(110) and Cu(111) has been studied in detail by Bent and coworkers [7]. Experimental evidence suggests that at low coverages disproportionation of surface methyl groups occurs to produce methane and methylene. The rate-determining step in this reaction sequence is shown to be the  $\alpha$ -elimination of methyl groups to produce adsorbed H and  $CH_2$ ; at high surface coverages direct C–C coupling reactions to produce higher hydrocarbons are found to predominate.

On Pt(111) methyl groups have been produced by the thermal and photochemical decomposition of adsorbed methyl halides [8–11]. Surface methyl with a  $C_{3v}$  or lower symmetry have been observed by high resolution electron energy loss spec-

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troscopy (HREELS) and reflection-absorption infrared spectroscopy (RAIRS). Studies carried out by Zaera et al. on the thermal chemistry of methyl iodide on Pt(111) [11] indicate that surface methyl undergoes either hydrogenation to form gas-phase methane or dehydrogenation to form surface carbon. The partitioning of methyl groups between these two reaction routes depends upon the surface coverage of methyl and hydrogen. Additional infrared data is also presented as evidence for the conversion of methyl groups to methylene above 260 K. No evidence for the existence of any C-C coupling reactions were found in this study.

However, there is a shortcoming associated with using methyl halides as the precursor for methyl groups, notably that dissociation of the precursor molecule produces an equal concentration of halogen atoms on the surface. In most cases these halogen atoms remain on the surface in the temperature region under investigation. The major effect of this coadsorbate is to block surface sites and thus set an upper limit on the obtainable methyl coverage. Undesirable secondary reactions between adsorbed methyl groups and halogen atoms are another potential problem as have been observed in the reaction of  $\text{CH}_3$  and Br on Pt(111) leading to the production of HBr [10]. A different approach is used in the present study to introduce methyl groups onto the Pt(111) surface. By generating methyl radicals through pyrolysis of azomethane it is possible to directly adsorb gas-phase methyl radicals [12]. This allows us to produce higher methyl radical coverages where C-C coupling reactions are more favored, in the absence of any surface halogen atoms. The surface chemistry of methyl groups adsorbed on Pt(111) has been studied using temperature programmed desorption (TPD) and RAIRS.

## 2. Experimental

All experiments were carried out at the University of Illinois at Chicago in a UHV system that has been described elsewhere [13]. In brief, it consists of a stainless steel chamber equipped

with a dedicated FTIR spectrometer (RS1, Mattson Instruments), a quadrupole mass spectrometer, and an Auger electron spectrometer. The chamber is pumped with a turbomolecular pump backed by a diffusion pump to a base pressure below  $2 \times 10^{-10}$  Torr. The Pt(111) single crystal was mounted onto a UHV manipulator, via two tungsten wires attached to power supply leads, and cooled by liquid nitrogen. This allows the sample temperature to be varied between 81 and 1000 K as measured by a chromel-alumel thermocouple spot-welded to the top-edge of the crystal. Sample cleaning was carried out by ion bombardment followed by several high temperature (750 K) annealing cycles in oxygen until the surface was judged clean by Auger electron spectroscopy.

The reactions of methyl groups on the Pt(111) surface were studied by annealing the surface and monitoring either the desorption products using the mass spectrometer or the associated changes in the infrared spectrum of the surface layer. In a temperature programmed desorption (TPD) experiment the surface was exposed to methyl radicals at 150 K, and then heated to 750 K at a constant heating rate of 1.5 K/s. Computer control of the mass spectrometer allowed for the collection of up to seven masses for each TPD run. In an infrared experiment, a background IR spectrum of the clean surface was recorded at the adsorption temperature (150 K) prior to exposing the surface to methyl radicals. The sample was then annealed to a known temperature and immediately cooled back to 150 K where another IR spectrum was taken. This procedure was then repeated for a series of increasing annealing temperatures. The spectra reported in this work were recorded using a narrow band MCT detector with a low wavenumber cutoff of  $800 \text{ cm}^{-1}$ , resolution of  $4 \text{ cm}^{-1}$ , and 2048 scans.

The methyl radicals used in this study were produced from a radical source based on the pyrolysis of azomethane as described previously [14]. In addition to methyl radicals, the dosing gas was made up of argon and the pyrolysis products nitrogen, methane, ethane and hydrogen (see table 1). Of these species, argon, nitrogen, methane and ethane desorb from the Pt(111)

Table 1  
Gas phase product yield relative to nitrogen from the methyl radical source employed

Product	Yield
Ar	3.60
N <sub>2</sub>	1.00
CH <sub>3</sub>	0.32
CH <sub>4</sub>	0.48
C <sub>2</sub> H <sub>6</sub>	0.50
H <sub>2</sub>	0.50

surface below 150 K. Hydrogen undergoes dissociative chemisorption on Pt(111) to form surface bound atomic hydrogen. In short, the source employed in this study leads to the adsorption of two chemically active species on the surface, methyl radicals and hydrogen. Therefore, the current study of the methyl surface chemistry was subject to the influence of surface hydrogen. where quoted, exposures were based on the partial pressure of methyl radicals. Table 1 shows the relative composition of gas phase products resulting from the particular source employed in this study.

### 3. Results

Figs. 1 and 2 depict the thermal desorption spectra of methane and hydrogen respectively, as a function of methyl radical exposure ( $1 \text{ L} = 10^{-6} \text{ Torr for 1 s}$ ). The only other desorption product

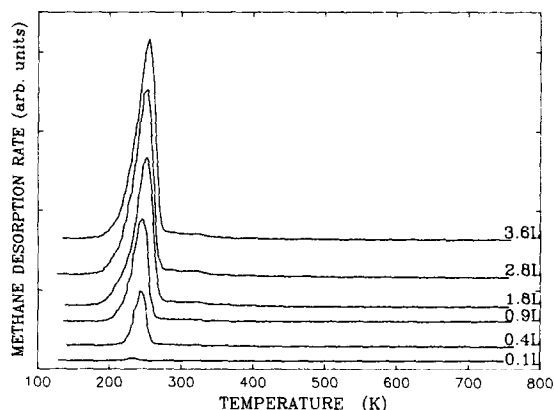


Fig. 1. Thermal desorption of methane after methyl radical adsorption at 150 K as a function of initial exposure.

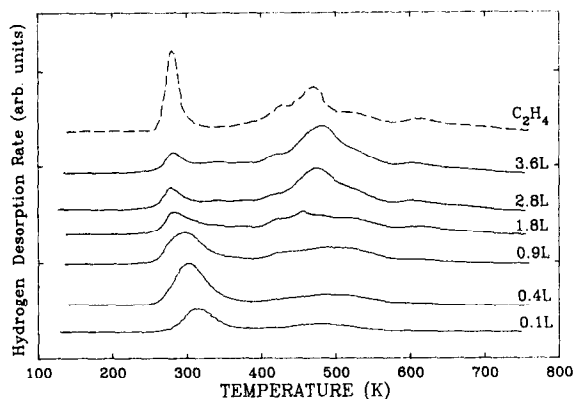


Fig. 2. Thermal desorption of hydrogen after methyl radical exposure at 150 K as a function of initial exposure. The top spectra corresponds to the hydrogen desorption profile for a saturation exposure of ethylene dosed at 150 K.

observed is CO, which arises from background adsorption, and is evolved at around 400 K. Fig. 1 shows that methane was produced in a narrow temperature range between 250–270 K, from the combination of surface methyl and hydrogen. This hydrogen could arise from two possible sources: from dissociative adsorption of H<sub>2</sub> in the dosing gas at 150 K or as the result of methyl dehydrogenation. The existence of a dehydrogenation reaction is required by the presence of CH<sub>x</sub> ( $x < 3$ ) species which give rise to the higher temperature hydrogen peaks seen at all methyl coverages. Hydrogen thermal desorption spectra as a function of increasing methyl coverage are shown in fig. 2. For comparison the hydrogen desorption profile corresponding to a saturation coverage of ethylene, as measured from hydrogen TPD, dosed onto Pt(111) at 150 K is also shown. Hydrogen desorption from a Pt(111) surface exposed to methyl radicals occurs in two separate temperature regimes, around 300 K and above 350 K. The lower temperature feature, which dominates at low methyl radical exposures corresponds to the second-order recombination of surface hydrogen atoms. These hydrogen atoms originate from methyl group dehydrogenation and H<sub>2</sub> adsorption. Hydrogen desorption at higher temperatures ( $> 350 \text{ K}$ ) originates from hydrocarbon dehydrogenation. At low coverages the spectra above 350 K are broad and featureless with a

maximum near 500 K. At higher initial methyl coverages additional features become more prominent, until saturation is reached ( $\sim 4$  L).

Fig. 3 shows RAIRS results for  $\text{CH}_3/\text{Pt}(111)$  at 150 K as a function of initial methyl radical exposure. The  $2885\text{ cm}^{-1}$  band, due to the symmetric stretch [15–17], grows in intensity and broadens to the high frequency side as a function of increasing  $\text{CH}_3$  coverage. Also seen in fig. 3 is a weak band at  $2750\text{ cm}^{-1}$  due to the first overtone of the asymmetric deformation in Fermi resonance with the  $2885\text{ cm}^{-1}$  symmetric stretch fundamental [15,17]. The absence of the asymmetric  $\text{CH}_3$  stretch and other asymmetric fundamentals suggests that the  $\text{CH}_3$  is adsorbed with  $\text{C}_{3v}$  symmetry. Although the symmetric  $\text{CH}_3$  deformation fundamental would also be symmetry allowed it appears to have an unobservably low intensity. In support of this interpretation, the HREELS dipole scattering intensity of this mode has been reported to be very weak [10]. The position of the  $\text{CH}_3$  symmetric stretch, the frequency and intensity of the  $2750\text{ cm}^{-1}$  peak relative to the  $2885\text{ cm}^{-1}$  band and the absence of all other bands including the symmetric  $\text{CH}_3$  deformation fundamental are in complete agreement with the RAIRS data acquired in this laboratory for  $\text{CH}_3/\text{Pt}(111)$  obtained through thermal decomposition of adsorbed  $\text{CH}_3\text{I}$  [15]. Within the

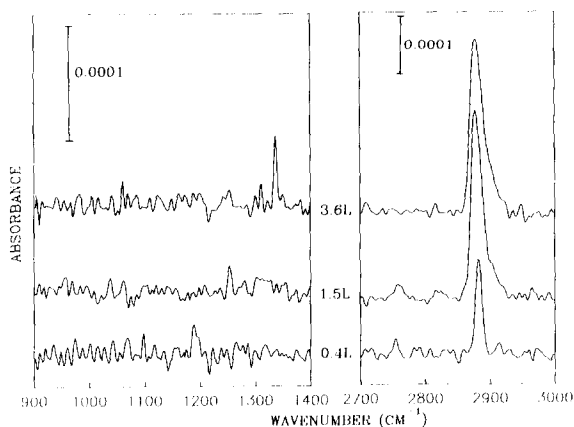


Fig. 3. Reflection-absorption infrared spectra for methyl radical chemisorbed on Pt(111) at 150 K as a function of initial exposure.

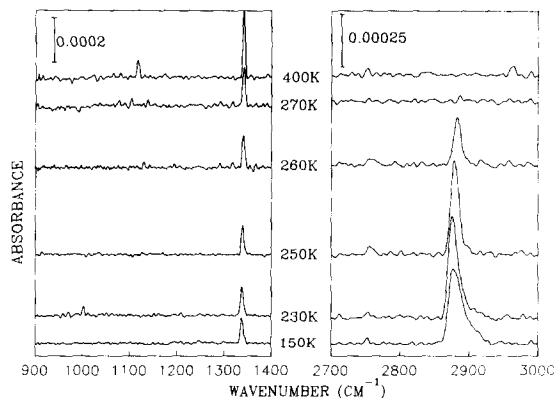


Fig. 4. Reflection-absorption infrared spectra for a saturation coverage of methyl radicals chemisorbed on Pt(111) at 150 K as a function of annealing temperature.

C–H deformation region ( $800\text{--}1500\text{ cm}^{-1}$ ) no reproducible bands are observed until methyl exposures greater than 3 L are used at which point a weak but reproducible peak at  $1339\text{ cm}^{-1}$  is observed. The intensity of this peak continues to increase until a saturation methyl coverage is reached. The frequency and narrowness (FWHM of  $\sim 5\text{ cm}^{-1}$ ) are characteristic of ethylidyne on Pt(111) [17]. (The  $\sim 5\text{ cm}^{-1}$  FWHM measured here with  $4\text{ cm}^{-1}$  resolution is consistent with the FWHM of  $\sim 2\text{ cm}^{-1}$  reported earlier using  $0.5\text{ cm}^{-1}$  resolution [17].)

Fig. 4 shows the RAIR spectra for a saturation exposure of methyl radicals as a function of annealing temperature. Upon annealing the surface to 230 K there is very little change in the peak intensity although fig. 4 clearly shows that the peak width of the  $\text{CH}_3$  symmetric stretch narrows considerably. Between 230–270 K the signal intensity falls rapidly until by 270 K there are essentially no methyl groups remaining on the surface. No other C–H stretching modes consistent with methylene or ethylidyne formation are observed at these elevated temperatures ( $> 230\text{ K}$ ) irrespective of initial methyl coverage. However, the decrease in methyl group coverage is accompanied by an increase in the ethylidyne coverage as indicated by ethylidyne peaks ( $\delta_{\text{CH}_3}$  at  $1339\text{ cm}^{-1}$  and  $\nu_{\text{CC}}$  at  $1115\text{ cm}^{-1}$ ). The ethyli-

dyne produced by heating is also seen to increase with initial methyl coverage.

#### 4. Discussion

Our results from TPD and IRAS experiments enable us to develop a picture of the surface chemistry of methyl groups on Pt(111). At 150 K methyl radicals, along with hydrogen, adsorb on the surface. The existence of methyl groups is confirmed by observation of a symmetric C-H stretching mode consistent with an adsorbed  $\text{CH}_3$  species. The breadth of this band at high coverages arises from a variety of local bonding environments on the surface following exposure to the methyl radical source. Indeed the peak narrowing which occurs upon annealing to 230 K suggests that the overlayer becomes more homogenous as the surface mobility of the adsorbed species increases.

IR/TPD data show that methyl groups are unstable on Pt(111) above 230 K, reacting with hydrogen to produce methane or dehydrogenating to produce  $\text{CH}_x$  ( $x < 3$ ) species. The partitioning between these two reaction pathways is found to vary with initial methyl and hydrogen coverage. A detailed discussion of the kinetics of these reactions will be the subject of a future publication [18]. Information on the chemical composition of the  $\text{CH}_x$  can be obtained by a comparison of the  $\text{H}_2$  TPD spectra (above 350 K) to those for known surface hydrocarbon species. At low methyl coverages the hydrogen TPD exhibits a single broad peak which is very similar to that found for  $\text{CH}_3\text{I}$ . As for  $\text{CH}_3\text{I}$ , this feature can be assigned to the dehydrogenation of  $\text{CH}_2$  to eventually yield surface carbon [11]. At higher methyl coverages distinctive high temperature features develop, similar to those reported for decomposition of  $\text{C}_2$ - $\text{C}_4$  hydrocarbon species (e.g. ethylene) adsorbed on Pt(111) [19]. This change in desorption profile supports the idea of lower temperature C-C coupling reaction(s) which become important only at high methyl coverages analogous to the situation seen on Cu(110) and Cu(111) [7]. In order to calibrate the amount of desorbing hydrogen which could be associated

with the ethylidyne produced, separate TPD/RAIRS experiments were carried out using ethylene, which is known to form exclusively ethylidyne on Pt(111). By annealing the surface to 400 K to produce ethylidyne it was possible to calibrate the IR intensity of the methyl umbrella deformation mode of ethylidyne to the amount of hydrogen which desorbs as the result of its higher temperature decomposition to yield surface carbon. These experiments showed that the ethylidyne produced as a result of the adsorption of methyl radicals and their subsequent surface chemistry accounts for approximately 25% of the hydrogen desorption associated with the additional higher coverage, high temperature features. It is therefore clear that the surface chemistry of the adsorbed methyl groups at high coverages produces additional hydrocarbon species other than methylene and ethylidyne, while we cannot specify the nature of this additional  $\text{C}_x$  hydrocarbon species formed by C-C coupling on the surface, we can eliminate any species whose surface chemistry involves ethylidyne as a product. Thus  $\text{C}_2\text{H}_4$  [20,17b],  $\text{CH}_2\text{CH}_3$  [21],  $\text{CHCH}_3$  [22], and  $\text{CHCH}_2$  [23] may all be ruled out leaving CCH and  $\text{CCH}_2$  as the only possible hydrogenated  $\text{C}_2$  species resulting from C-C coupling. Of course other higher order hydrocarbons may also be present to account for the high temperature hydrogen desorption profiles observed at high methyl exposures.

The unexpected observation of ethylidyne formation at 150 K, for high initial methyl coverages, indicates that C-C coupling is possible even at low temperatures where Pt is unable to effectively produce labile C-H bonds. The mechanism for ethylidyne formation is unknown at present but may arise from the direct reaction of incoming methyl groups with any small amount of carbidic carbon remaining on the surface after cleaning.

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## References

- [1] S.A. Costello, B. Roop, Z.-M. Liu and J.M. White, *J. Phys. Chem.* 92 (1988) 1019.
- [2] E.P. Marsh, F.L. Tabares, M.R. Schneider, T.L. Gilton, W. Meier and J.P. Cowin, *J. Chem. Phys.* 92 (1990) 2004.
- [3] L.-X. Zhou and J.M. White, *Surf. Sci.* 241 (1991) 270.
- [4] A. Berko and F. Solymosi, *J. Phys. Chem.* 93 (1989) 12.
- [5] J.G. Chen, T.P. Beebe Jr., J.E. Crowell and J.T. Yates Jr., *J. Am. Soc.* 109 (1987) 1726.
- [6] S.T. Ceyer, *Langmuir* 6 (1990) 82.
- [7] (a) B.E. Bent, R.G. Nuzzo and L.H. Dubois, *J. Am. Chem. Soc.* 111 (1987) 1726;  
(b) J.-L. Lin and B.E. Bent, *J. Vac. Sci. Technol. A* 10 (1992) 2202.
- [8] M.A. Henderson, G.E. Mitchell and J.M. White, *Surf. Sci.* 184 (1987) L325.
- [9] Z.-M. Liu, S. Akhter, B. Roop and J.M. White, *J. Am. Chem. Soc.* 110 (1988) 8708.
- [10] G. Radhakrishnan, W. Stenzel, R. Hemmen, H. Conrad and A.M. Bradshaw, *J. Chem. Phys.* 95 (1991) 3930.
- [11] (a) F. Zaera, *Langmuir* 7 (1991) 1998;  
(b) F. Zaera and H. Hoffmann, *J. Phys. Chem.* 95 (1991) 6297.
- [12] G.H. Smudde Jr., X.D. Peng, R. Viswanathan and P.C. Stair, *J. Vac. Sci. Technol. A* 9 (1991) 1885.
- [13] N.E. Brubaker and M. Trenary, *J. Chem. Phys.* 85 (1986) 6100.
- [14] X.D. Peng, R. Viswanathan, G.H. Smudde, Jr and P.C. Stair, *Rev. Sci. Instrum.* 63 (1992) 3930.
- [15] J. Fan and M. Trenary, *J. Chem. Phys.* 39 (1987) 589.
- [16] N. Sheppard, *Ann. Rev. Phys.* 39 (1987) 589.
- [17] (a) I.J. Malik, M.E. Brudaker, S.B. Moshin and M. Trenary, *J. Chem. Phys.* 87 (1988) 5554;  
(b) I.J. Malik, V.Y. Agrawal and M. Trenary, *J. Chem. Phys.* 89 (1988) 3861.
- [18] D.H. Fairbrother, X.D. Peng, P.C. Stair and M. Trenary, in preparation.
- [19] M. Salmeron and G.A. Somorjai, *J. Phys. Chem.* 86 (1982) 341.
- [20] (a) L. Kesmodel, L. Dubois and G.A. Somorjai, *J. Chem. Phys.* 70 (1979) 2180.
- [21] F. Zaera, *Surf. Sci.* 219 (1989) 453.
- [22] A.M. Baro and H. Ibach, *J. Chem. Phys.* 74 (1981) 4194.
- [23] F. Zaera, *J. Am. Chem. Soc.* 111 (1989) 4240.