Hydrogenolysis of adsorbed methylthiolate on the Pt(111) surface

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A combination of temperature programmed reaction experiments and fluorescence yield near edge spectroscopy (FYNES) has been used to characterize hydrogen induced C–S bond activation in adsorbed methylthiolate on the Pt(111) surface. The low temperature methane peak observed at 310 K during temperature programmed decomposition of methanethiol clearly involves reaction with adsorbed hydrogen since deuterium incorporation is observed in the presence of coadsorbed deuterium. Some multiple deuteration is observed suggesting that a mixture of carbon containing species may be involved in the hydrogenolysis process. In situ FYNES above the carbon K edge has been used to characterize the kinetics of this hydrogenolysis process in more detail. Transient FYNES measurements were used to characterize changes in the total carbon concentration during the hydrogenolysis reaction. In situ temperature programmed reaction experiments performed in 0.02 Torr of hydrogen clearly indicate that hydrogenolysis begins near 290 K and all carbon containing species are removed by 360 K. In situ isothermal kinetic studies indicate that the hydrogenolysis reaction is first order in adsorbed thiolate coverage and approximately half order in hydrogen pressure. The apparent activation energy for the hydrogenolysis reaction is 18 kcal/mol in the presence of 0.02 Torr of gaseous hydrogen. This activation energy represents a lower bound for the hydrogenolysis activation energy since the apparent heat includes the heat of adsorption for hydrogen. These direct kinetic measurements of this hydrogenolysis reaction under reactive gaseous environments highlight the role that in situ methods can play in characterizing surface reaction processes.

1. Introduction

Despite the growing importance of catalytic hydrodesulfurization in fuel processing, few fundamental studies of C–S hydrogenolysis on surfaces have appeared in the literature. The overall sulfur content in petroleum feedstocks continues to increase as clean petroleum reserves are depleted [1]. Thus hydrodesulfurization of petroleum feedstocks will play an increasingly important role in a broad range of refining processes. Because of their involvement as potential intermediates in hydrodesulfurization processes and their structural simplicity, thiols (R–S–H) are interesting model reactants for a range of catalytic desulfurization processes. Recently, adsorption, dehydrogenation and decomposition of a range of

thiols has been characterized by several groups on clean, oxided and sulfided metal surfaces. The adsorption, dehydrogenation and decomposition of methanethiol (CH_3SH) has been investigated on a number of metal single crystal surfaces including: Pt(111) [2], Ni(100) [3,4], Ni(110) [5], Fe(100) [6], Cu(100) [7], Cu(111) [4,8], Au(111) [9], W(211) [10]. Thermal decomposition of higher thiols on the Mo(110) surface has also been recently characterized by Roberts and Friend [11–15].

Methanethiol adsorption and dehydrogenation on the Pt(111) surface were characterized by Koestner et al. [2] in vacuum using a combination of high resolution electron energy loss spectroscopy (HREELS), temperature programmed desorption measurements (TPD), and ultra-soft X-ray absorption detected via partial electron yield. These authors have determined the structure and orientation of methylthiolate (CH_3S)

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and methylenesulfide (CH_2S) surface intermediates formed during thermal decomposition of adsorbed methanethiol. Specifically, adsorbed methylthiolate (CH_3S) was observed at 255 K with the C–S bond oriented at about 45° relative to the surface. In contrast to several other more active metal surfaces [5,6,10], adsorbed CH_3 and CH_2 were not observed on the Pt(111) surface during decomposition of methylthiolate below 400 K. Instead, dehydrogenation of the methylthiolate appears to dominate below 400 K resulting in the formation of methylenesulfide. This intermediate is adsorbed with the C–S axis at approximately 20° relative to the surface. Above 400 K methylenesulfide decomposes to form methane and ethylene at 430, and hydrogen at 520 K.

2. Experimental

A combination of temperature programmed reaction experiments and fluorescence yield ultra-soft X-ray absorption measurements have been used to characterize hydrogenolysis of adsorbed methylthiolate on the Pt(111) surface. The in situ capabilities of the fluorescence yield ultra-soft X-ray absorption method have been utilized to facilitate temperature programmed reaction and isothermal kinetic experiments involving the hydrogenolysis of adsorbed methylthiolate in 0.02 Torr of gas phase hydrogen. The experiments have been performed in two vacuum systems. The first is equipped with capabilities for multiple mass temperature programmed reaction and desorption experiments, directional dosing of hydrogen, low energy electron diffraction, and Auger electron spectroscopy. The second system is equipped with these same surface spectroscopies, as well as a reaction chamber equipped for in situ fluorescence yield near edge spectroscopy (FYNES) studies at elevated pressure. The reaction chamber is isolated from the UHV beam line and the synchrotron by X-ray windows which are transparent in the ultra-soft X-ray region. X-ray absorption by the surface was measured using a high performance fluorescence de-
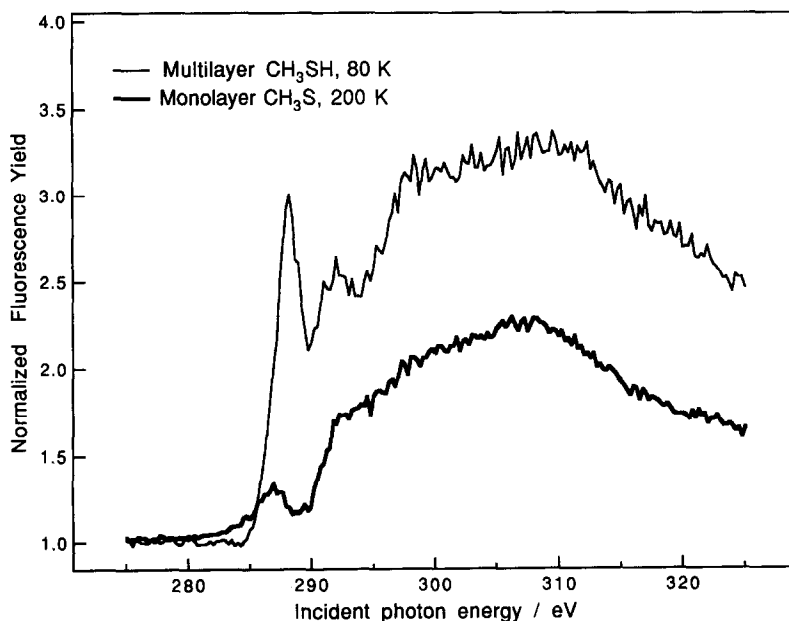

Fig. 1. Fluorescence yield reference spectra for solid methanethiol, and a monolayer of the methylthiolate surface intermediate on the Pt(111) surface. The multilayer spectrum has been corrected for contributions from the monolayer. Both spectra were taken at normal beam incidence. The C–S resonance is about 288 eV and the carbon "atomic" edge is near 290 eV. The isothermal kinetic experiments were done in the continuum at 315 eV so that the total carbon content on the surface could be characterized.

tector optimized for carbon fluorescence measurements [16–18]. Details of the experimental apparatus and fluorescence detector have been described previously [19–21].

2.1. Fluorescence yield experiments

To avoid potential difficulties arising from the sensitivity of the near edge X-ray absorption cross sections to the bonding and orientation of adsorbed species, non-resonant continuum ultra-soft X-ray absorption 30 eV above the carbon K edge was used to determine the concentration of adsorbed carbon containing species during many of these kinetic experiments. Specifically, the intensity of carbon fluorescence resulting from excitation at normal incidence with an energy of 315 eV was used as a measure of the concentration of all carbon containing surface species. Detailed studies of FYNES [18] have demonstrated that this technique is capable of detecting 0.02 monolayer (ML) (or about 3×10^{13} carbon atoms/cm^2). Reference fluorescence yield spectra of thin solid multilayer of methanethiol and a monolayer of the methylthiolate surface intermediate adsorbed on the Pt(111) surface are shown in fig. 1. Note the C–S resonance near 288 eV and the "atomic" carbon edge which appears near 290 eV in both the reference spectra. The monolayer of methylthiolate was formed by heating a methanethiol saturated surface to 200 K. The fluorescence yield signal from this annealed methylthiolate layer was used as an internal standard for monolayer carbon coverages for the FYNES kinetic measurements. The sulfur in the adsorbed thiol remains on the surface in atomic form after the hydrogenolysis reaction is complete. This atomic sulfur forms a (2×2) overlayer structure indicating that approximately 0.25 ML of sulfur were deposited from a saturated monolayer of methanethiol. The carbon content of a saturated methanethiol monolayer is therefore approximately 0.25 ML. Post reaction Auger characterization of the surface reveals that no carbon containing species remain on the surface for hydrogen pressures above 2×10^{-4} Torr and temperatures above 300 K. Thus each kinetics experiment contains an independently verified zero carbon coverage standard.

2.2. Temperature programmed fluorescence yield experiments

A set of temperature programmed fluorescence yield experiments were performed in 0.02 Torr of hydrogen to characterize the temperature range and extent of hydrogenolysis for adsorbed methylthiolate on the Pt(111) surface. The Pt(111) surface was first saturated with methanethiol (CH$_3$SH) at 100 K and heated to 200 K to remove multilayers of methanethiol and to form a monolayer of adsorbed methylthiolate from molecular methanethiol. This monolayer of methylthiolate (CH$_3$S) was then cooled to 100 K before the TPR experiments were initiated. During the hydrogenolysis experiment the carbon fluorescence yield was monitored, (1) at the C–S resonance at 288.2 eV to determine the rate of C–S bond activation and (2) in the carbon continuum region at 315 eV to determine the extent of carbon removal. The fluorescence yield at 288 eV depends both on the orientation and concentration of the C–S bond on the surface, while the fluorescence signal at 315 eV depends primarily on the concentration of all carbon containing species on the surface. An internal coverage standard was collected for 1–2 min before each experiment began. The pressure and fluorescence signal were allowed to equilibrate for approximately 4–6 min after 0.02 Torr of H$_2$ was introduced. The sample was then heated at 0.5 K/s up to 750 K while continuously monitoring the fluorescence yield at a single incident photon energy (288 or 315 eV).

2.3. Isothermal fluorescence yield experiments

A set of isothermal kinetic experiments at 305, 315 and 330 K were performed to determine the kinetics of C–S bond hydrogenolysis on the Pt(111) surface. The Pt(111) surface was first saturated with methanethiol (CH$_3$SH) at 100 K. A monolayer containing primarily adsorbed methylthiolate (CH$_3$S) was formed by annealing the surface to 200 K for 2 min. This surface was

then cooled to 100 K before the hydrogenolysis experiments were initiated. During the hydrogenolysis experiment the carbon fluorescence yield was monitored for 1–2 min before the experiment was initiated as an internal standard. The pressure and fluorescence signal were allowed to equilibrate for approximately 4–6 min after 0.02 Torr of H_2 was introduced. The sample was then heated at 10 K/s to the indicated reaction temperatures (e.g. 330 K). This "abrupt" thermal initiation sequence took at most 20–30 s. The sample temperature was maintained at reaction temperature for 900–1200 s to insure that the reaction was complete. To confirm the internal zero coverage standard for carbon the sample was then heated in hydrogen to 750 K for approximately 100 s. Details of similar experimental procedures involving the displacement of CO with hydrogen are discussed in previous papers [22–24].

3. Results and discussion

A combination of temperature programmed reaction experiments and fluorescence yield ultra-soft X-ray absorption measurements have been used to characterize the hydrogenolysis of methylthiolate adsorbed on the Pt(111) surface. The structure and bonding of methylthiolate and methylenesulfide formed by dehydrogenation of adsorbed thiolate during vacuum annealing experiments were the primary focus of previous work on the Pt(111) surface [2]. The experiments reported here are focused on hydrogenolysis of methylthiolate on the Pt(111) surface in the 290–330 K temperature range. The onset of methane formation is observed in the 290 K region during temperature programmed decomposition and reaction of methanethiol. The low temperature methane peak at 310 K during temperature programmed decomposition of methanethiol clearly
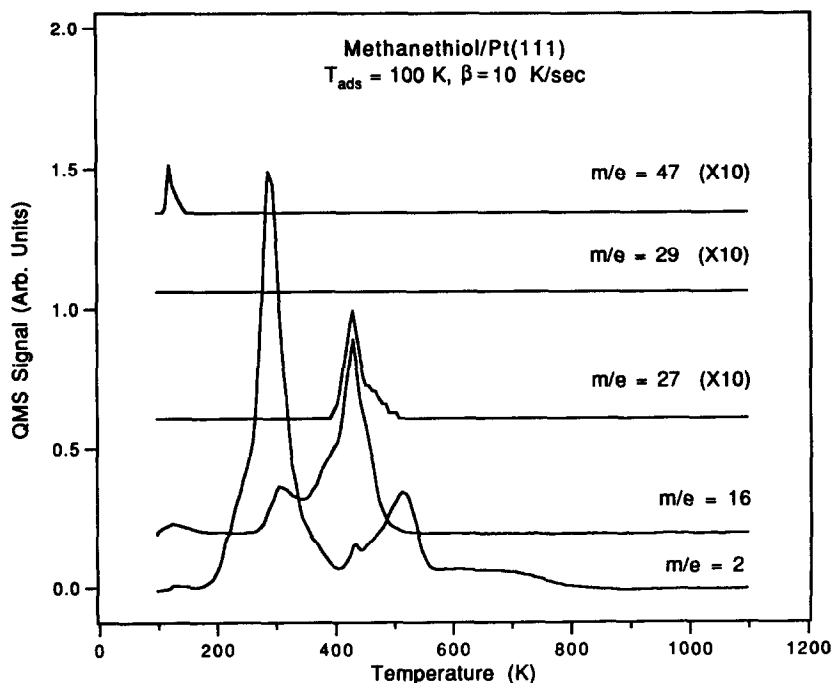

Fig. 2. A vacuum TPD spectrum from slightly more than a monolayer of adsorbed methanethiol on the Pt(111) surface. Hydrogen, methane and ethylene are the primary reaction products observed. All the sulfur from the initial methanethiol and approximately half of the original carbon remain on the surface after heating to 1000 K. The heating rate was 10 K/s and the adsorption temperature was 100 K.

involves reaction with coadsorbed hydrogen since deuterium incorporation is observed at 310 K in the presence of coadsorbed deuterium. Complete hydrogenolysis of the adsorbed thiolate can be achieved in 0.02 Torr of hydrogen both during temperature programmed and isothermal kinetic studies. The sulfur from the adsorbed thiolate remains on the surface, while methane formation appears to be the primary carbon removal pathway.

3.1. Temperature programmed reaction studies

A desorption spectrum of adsorbed methanethiol is shown in fig. 2. Hydrogen, methane and ethylene are the primary decomposition products observed. No ethane formation is observed. Methane formation peaks which must involve C–S bond activation are observed at 310 and 430 K. The low temperature methane formation process at 310 K is the primary reaction channel which is discussed in this paper

A paper focused on the TPD/TPR experiments and associated isotopic studies is being published separately because of the complexity of the surface reactions observed [25]. For completeness, a brief discussion of the high temperature C–S bond activation processes follows. The peak shape of the ethylene peak at 430 K is very similar to the methane peak at this same temperature. The coverage dependence of the total yield of these two competitive processes at 430 K is also quite similar. These similarities coupled with isotope studies indicate that these competitive mechanisms involve the same surface intermediate, probably adsorbed methylenesulfide.

Fig. 3 shows the desorption products resulting from a reaction of a low coverage methanethiol (~ 40% saturated) which was subsequently exposed to 5 L of deuterium. This clearly illustrates that the first methane peak at 310 K involves reactions with surface hydrogen since deuterated methane is observed at 310 K in the presence of coadsorbed deuterium. Little or no deuterium incorporation is observed for either the methane or ethylene produced at 430 K, indicating that coadsorbed hydrogen does not play an important role in these high temperature processes. The
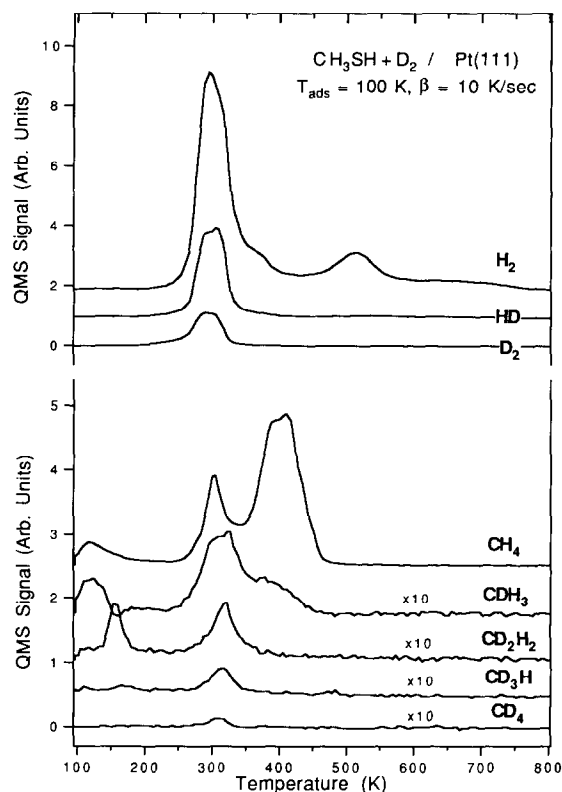
Fig. 3. TPD products resulting from reaction of a low coverage of methanethiol (~ 40% saturated) post exposed to 5 L of deuterium. Note that deuterium makes up a small fraction of the hydrogen desorbing from the surface near 300 K since substantial amounts of this hydrogen are produced by decomposition of the protic methanethiol. Singly and doubly deuterated methane are the dominant desorption products from the low temperature C–S bond activation process.

extent of deuterium incorporation for the 310 K methane product is 61% D_1, 28% D_2, 8% D_3 and 3% D_4. Deuterium incorporation may result from exchange between surface intermediates and coadsorbed deuterium prior to the actual hydrogenolysis step. These results can also be rationalized by considering deuterium addition to a mixture of adsorbed methylthiolate and methylenesulfide surface intermediates. We favor the latter mechanism because of the demonstrated stability of both the methylthiolate and methylenesulfide surface intermediates in this temperature range.

3.2. Temperature programmed hydrogenolysis studies

A series of temperature programmed kinetic experiments utilizing FYNES have been performed to further characterize the hydrogenolysis process. In order to evaluate the possibility that a distinguishable intermediate may participate in the low temperature hydrogenolysis process, temperature programmed measurements in 0.02 Torr of hydrogen were performed (fig. 4) using: (1) the molecular resonance at 288.2 eV characteristic of the C–S bond in adsorbed methylthiolate and methylenesulfide, and (2) continuum carbon fluorescence at 315 eV which is sensitive to the total amount of carbon on the surface. No temperature shifts or differential structures were observed within the signal to noise ratio of our

TP-FYNES measurements. This indicates that no distinguishable stable carbon containing surface intermediates are involved in this hydrogenolysis reaction. Unfortunately, both methanethiol and methylene sulfide have C–S resonances near 288 eV and are not expected to be distinguishable using this method. These studies of the hydrogenolysis reaction are consistent with our earlier spectroscopic studies [2] which indicate that methylthiolate (observed at 255 K) and methylenesulfide (observed at 400 K) are the two dominant surface intermediates on Pt(111) surface. We believe that with these high hydrogen pressures and temperatures in the 300 K regime, methylthiolate will be the dominant intermediate on the Pt(111) surface. Fig. 4 also shows that both C–S bond activation and carbon removal are almost complete by 360 K. In contrast, in the
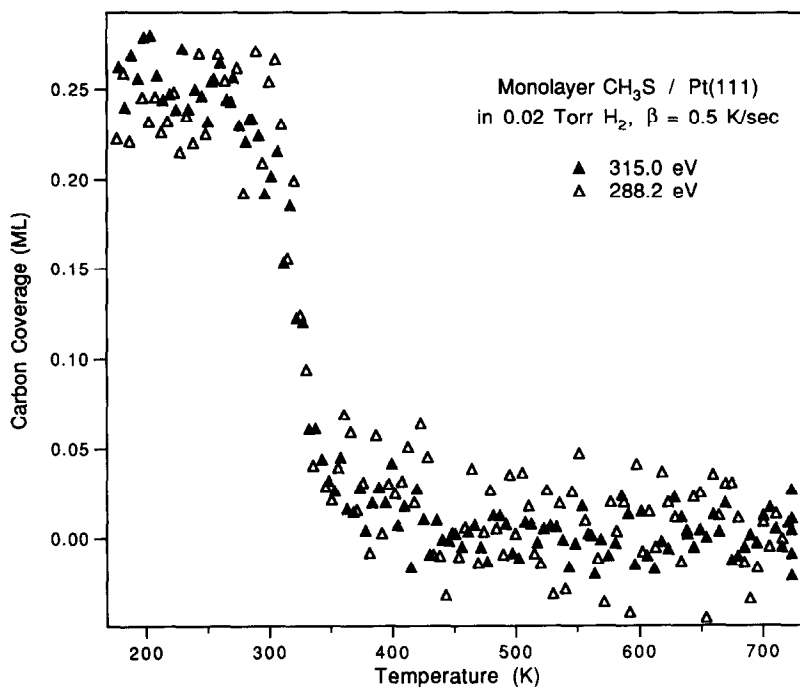

Fig. 4. In situ temperature programmed reaction studies of methylthiolate in 0.02 Torr hydrogen on the Pt(111) surface at 288.2 and 315 eV. Carbon fluorescence at 288.2 eV is sensitive to the amount and orientation of the C–S bonds on the surface. Carbon continuum fluorescence at 315 eV is sensitive to the total amount of carbon on the surface. The heating rate was 0.5 K/s. All of the carbon containing species are removed in the presence of hydrogen by 360 K.
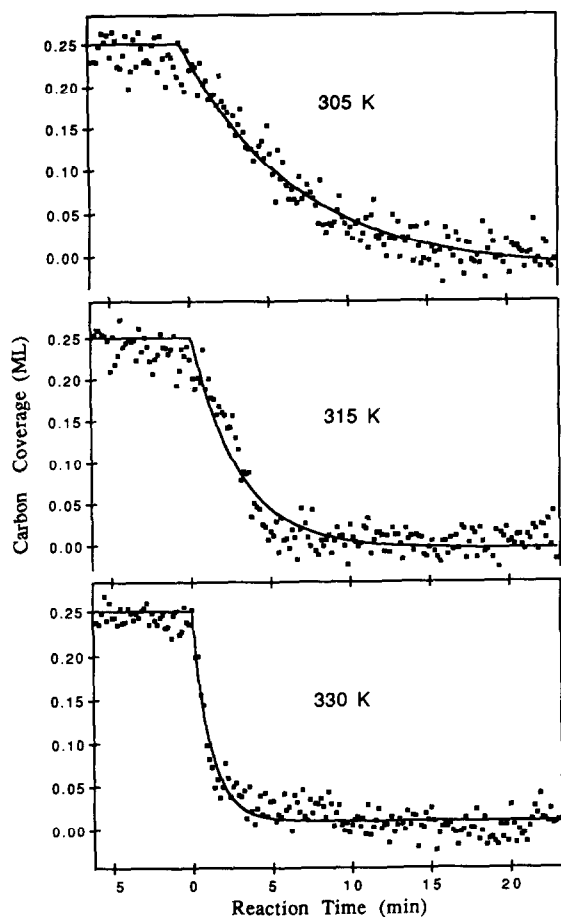
Fig. 5. A set of transient isothermal kinetic experiments for hydrogenolysis of methylthiolate on Pt(111) at 305, 315 and 330 K in the presence of 0.02 Torr of hydrogen. Reaction time was measured from the time when the indicated reaction temperature was attained by the sample. Single exponential fits of the form $\theta_t = \theta_\infty + \theta_0 \exp(-Kt)$ are also shown.

layers of adsorbed methylthiolate (CH_3S) on the Pt(111) surface for hydrogen pressures in the 2×10^{-4} to 2×10^{-2} Torr range over the 305 to 330 K temperature range.

In situ isothermal kinetic studies in the presence of 0.02 Torr of hydrogen for the Pt(111) surface at 305, 315 and 330 K are shown in fig. 5. The experimental data is fit by a single exponential of the form $\theta_t = \theta_\infty + \theta_0 \exp(-Kt)$. θ_t is the time dependent carbon coverage. θ_∞ is the carbon coverage at infinite time. θ_0 is the initial carbon
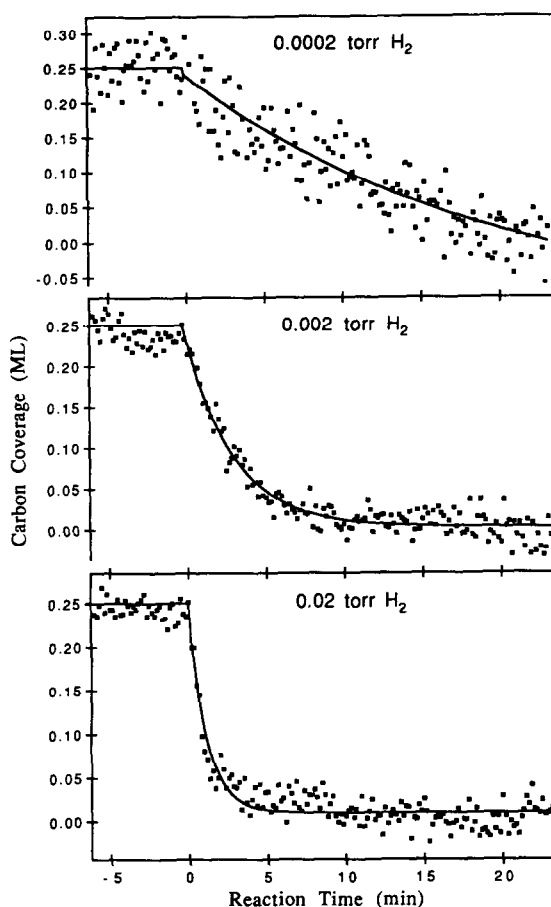

Fig. 6. A set of transient isothermal kinetic experiments for hydrogenolysis of methylthiolate on Pt(111) at 330 K over a range of hydrogen pressures. The hydrogen pressures were stabilized at 200 K. Reaction time was measured from the time when 330 K was attained by the sample. The single exponential fits of the form $\theta_t = \theta_\infty + \theta_0 \exp(-Kt)$ are also shown.

absence of hydrogen, a large fraction of the C–S bond scission does not occur until 450 K.

3.3. Isothermal hydrogenolysis studies

In order to characterize the kinetics of methylthiolate hydrogenolysis in more detail, a series of in situ isothermal kinetic studies on the Pt(111) surface were performed as shown in figs. 5 and 6. Isothermal temperature jump kinetic measurements have been used to characterize the hydrogenolysis kinetics of well characterized mono-

coverage. t is the time and K is the apparent activation energy for the carbon removal process in hydrogen. These experiments suggest that a single surface reaction is the rate limiting step for the hydrogenolysis reaction. Previous spectroscopic studies suggest that adsorbed methylthiolate is the dominant surface intermediate in this temperature range [2].

Carbon removal as a function of time on the Pt(111) surface at 330 K is shown in fig. 6 for a range of hydrogen pressures. These rate data were fitted by a first order exponential rate equation in surface carbon coverage. Analysis of the pressure dependence of the first order rate constants derived from fig. 6 indicate the reaction is about 0.6 order in hydrogen, suggesting that surface hydrogen is basically in equilibrium with gas phase hydrogen over this temperature and pressure range. Therefore, the hydrogen atom concentration is determined primarily by temperature and hydrogen pressure and changes very little as the reaction proceeds. This is not surprising since the sulfur from the thiolate hydrogenolysis remains on the surface. That is, the surface

hydrogen coverage is basically independent of the concentration of adsorbed carbon containing intermediates. The deviation from the ideal value of 0.5 hydrogen order is not large especially considering the signal to noise ratio of our rate data. Again, this kinetic data is consistent with a single rate limiting step involving reaction(s) with hydrogen atoms.

An Arrhenius plot for the rate constants determined from the exponential fits of the curves is shown in fig. 7. The slope gives an apparent activation energy of about 18 kcal/mol in presence of 0.02 Torr of hydrogen. This apparent activation energy represents a lower bound for the hydrogenolysis activation energy since the apparent heat includes the heat of adsorption for hydrogen. The relationship is simply given by:

$$E_{app} = E_{act} - (\Delta H_{ads})/2,$$

where E_{app} and E_{act} are the apparent and the actual activation energies. The high hydrogen coverages resulting from high hydrogen pressures and a large concentration of adsorbed sulfur will both reduce the expected isosteric heat of ad-
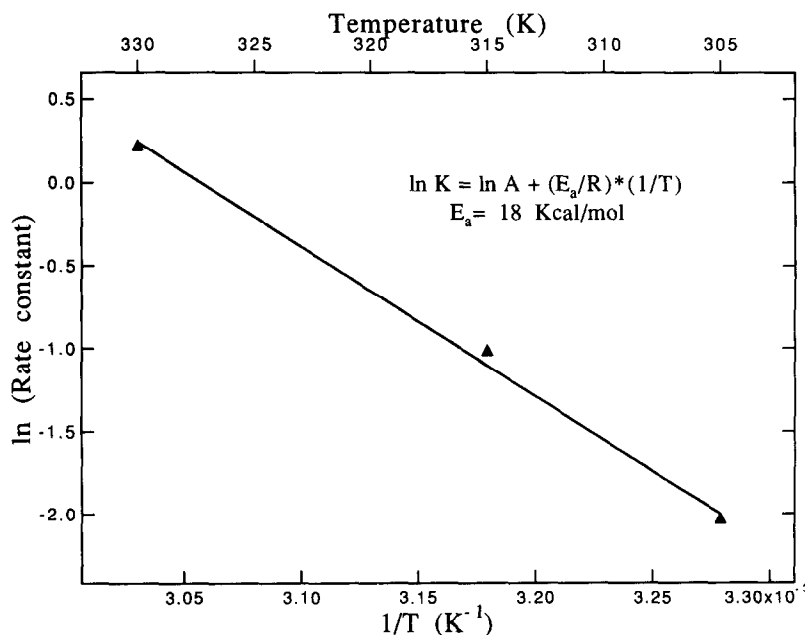

Fig. 7. An Arrhenius plot for the rate constants determined from the exponential fits of the curves shown in fig. 5. The slope gives an apparent activation energy of about 18 kcal/mol in presence of 0.02 Torr of hydrogen.

sorption for hydrogen, suggesting that the apparent activation energy should be similar to the actual activation energy of the hydrogenolysis process. Previous studies of hydrogen on the clean Pt(111) surface [26–28] indicate that the isosteric heats of adsorption for hydrogen are in the 6–16 kcal/mol range depending on hydrogen coverage. Decreased heats of adsorption in the 4–6 kcal/mol range have been proposed in the presence of sulfur [29].

4. Conclusion

A combination of temperature programmed reaction experiments and fluorescence yield ultra-soft X-ray absorption measurements were utilized to characterize the hydrogenolysis of methylthiolate adsorbed on the Pt(111) surface. The low temperature methane peak at 310 K during temperature programmed decomposition of methanethiol clearly involves reaction with coadsorbed hydrogen since deuterated methane is observed at 310 K in the presence of coadsorbed deuterium. The multiple deuteration observed suggests that a mixture of carbon containing species may be involved in the hydrogenolysis process, namely methylthiolate and methylenesulfide. In situ temperature programmed reaction experiments performed in 0.02 Torr of hydrogen clearly indicate that hydrogenolysis begins near 290 and is complete by 360 K. In situ isothermal kinetic studies indicate that the hydrogenolysis reaction is first order in adsorbed thiolate coverage and approximately half order in hydrogen pressure. The apparent activation energy for the hydrogenolysis reaction is 18 kcal/mol in the presence of 0.02 Torr of gaseous hydrogen. This activation energy represents a lower bound for the hydrogenolysis activation energy since the apparent heat includes the heat of adsorption for hydrogen. These direct kinetic measurements of this hydrogenolysis reaction under reactive gaseous environments highlight the role that in situ methods can play in characterizing surface reaction processes. This example also provides a severe test of transient ultra-soft X-ray absorption measurements since the continuum absorp-

tion has substantially smaller cross sections than the resonant molecular transitions.

Acknowledgement

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