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SURFACE SYNTHESIS OF THIOPHENE

T.M. GENTLE

Dow Corning Corporation, Midland, MI 48686, U.S.A.

C.T. TSAI, K.P. WALLEY and A.J. GELLMAN

School of Chemical Sciences, University of Illinois, Urbana, IL 61801, U.S.A.

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A cyclization reaction has been observed in which thiophene is produced from acetylene and sulfur co-adsorbed on the Pd(111) surface. As in the case of acetylene trimerization to benzene the reaction yielding thiophene can proceed via an intermediate species of stoichiometry C_4H_4. The ability of the reaction intermediate to extract sulfur from the surface varies between the two phases of adsorbed sulfur that can exist on the Pd(111) surface.

1. Introduction

A number of cyclization reactions involving molecules containing triple bonds have been observed over clean, crystalline surfaces of palladium. The mostly widely studied has been the trimerization of acetylene to benzene on the Pd(111) surface [1–6]. This reaction has been observed on all three low Miller index surfaces of palladium and under conditions ranging from ultra high vacuum to atmospheric pressures [4]. Other surface induced reactions of this type include the cyclization of acetylene with methylacetylene to form toluene and acetylene with hydrogen cyanide to form pyridine [5]. The acetylene cyclotrimerization reaction occurs without cleavage of CC bonds [6] and it has been shown that the reaction can proceed via a sequential mechanism involving an intermediate having C_4H_4 stochiometry [7,8].

The novel thiophene synthesis reaction reported in this letter has been observed following the adsorption of acetylene on a sulfided Pd(111) surface. The reaction exhibits a number of similarities to the acetylene trimerization reaction but with the added complication that the reaction is dependent on the nature of the sulfur atom at the surface. Studies of sulfur overlayers produced at low temperatures on the Pd(111) surface show that heating to temperatures in excess of 400 K results in an irreversible phase transition [9,10]. The transition results in complete disappearance of the low temperature $(\sqrt{3} \times \sqrt{3})$R30 LEED pattern and is thought to involve incorporation of sulfur into the Pd(111) surface. Although

the nature of the sulfur atom present at the surface is undetermined, the work described here indicates that it is chemically distinct from the low temperature species.

2. Experimental

The experiments reported in this letter have been performed in an ultrahigh vacuum chamber pumped to a base pressure of $< 5 \times 10^{-11}$ torr and equipped for LEED and Auger analysis of the surface. Adsorption was performed by allowing gas to leak into the chamber through collimated, capillary array dosers. The exposures cited are not corrected for the enhancement factor of the doser ($> 100\times$). Desorption was performed by resistive heating of the sample at a rate of ~ 12 K/sec in front of a Dycor M250M quadrupole mass spectrometer.

Sulfur overlayers were produced by exposure of the clean Pd(111) surface to 0.01 L H_2S (using a doser) at low temperature (< 170 K) followed by heating to either 300 K or 1000 K, depending upon which sulfur overlayer phase was to be produced. This procedure was repeated three times resulting in a surface which was saturated with sulfur in the sense that further repetition did not result in any increase in the sulfur Auger signal. The sulfur overlayers produced in this fashion from the $(\sqrt{3} \times \sqrt{3})R30°$ and $(\sqrt{7} \times \sqrt{7})R19°$ LEED patterns observed in earlier work in which S_2 was used to deposit sulfur [9]. These occur at coverages of $\theta_S = 0.33$ and $\theta_S > 0.62$ respectively. Acetylene adsorption was accomplished by exposure of the surface to 0.2 L C_2H_2 at low temperatures (< 170 K). On the clean surface the coverage resulting from this exposure was sufficient to saturate the reaction path leading to the formation of benzene. Previous work has shown that the trimerization reaction occurs only for acetylene coverages in excess of 0.33 monolayer, however, coverage needed to saturate this path is not well determined [1].

3. Results

3.1. THIOPHENE SYNTHESIS ON THE Pd(111)/S HIGH TEMPERATURE PHASE

The high temperature phase of the sulfur overlayer on a Pd(111) surface is produced by exposures to H_2S followed by heating to 1000 K. Figure 1 shows the desorption spectrum of both thiophene and benzene from this surface after exposure to C_2H_2. The reaction results in thiophene desorption in the temperature range 320 K–480 K. The product has been identified by comparison of its mass spectral fragmentation pattern with that of thiophene reversibly adsorbed to the surface.

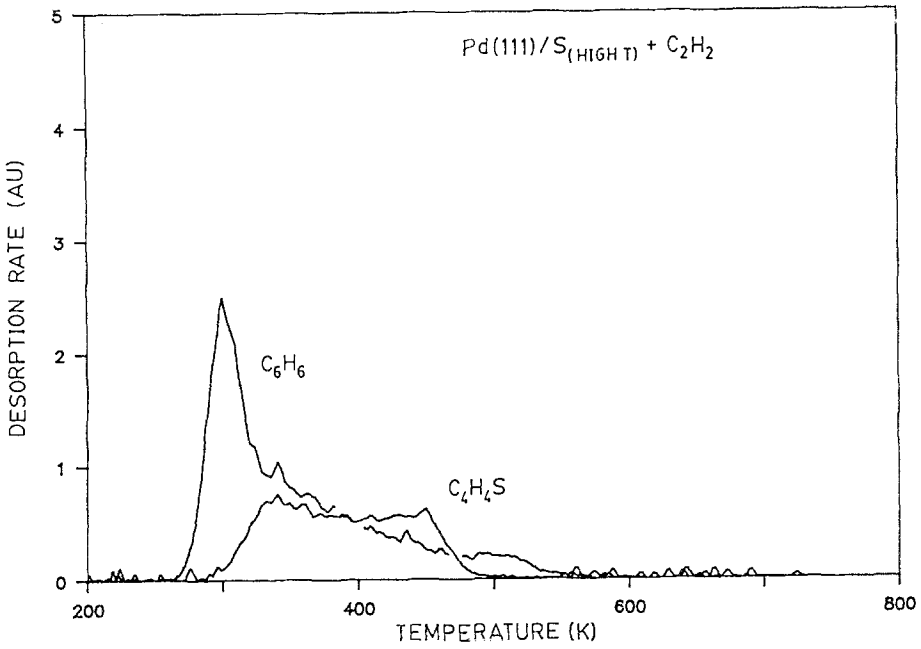

Fig. 1. Benzene (78 amu) and thiophene (84 amu) desorption following the adsorption (170 K) of C_2H_2 (0.2 L) on the high temperature phase of the Pd(111)/S surface.

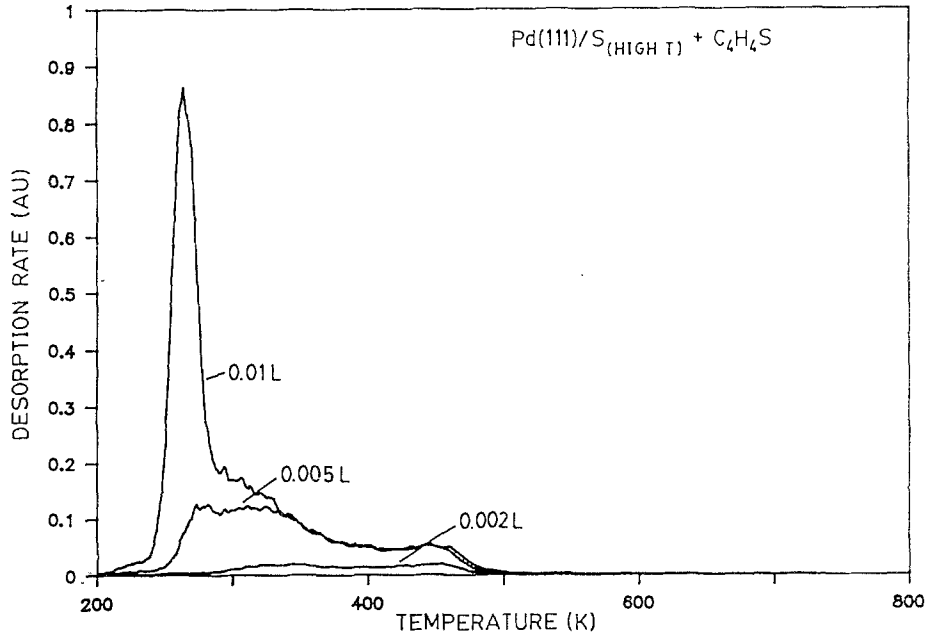

Fig. 2. Thiophene desorption from the high temperature phase of the Pd(111)/S surface following exposure to thiophene at 170 K. Multilayer formation begins at 0.05 L exposure.

In an attempt to determine the absolute yield of the thiophene from the reaction we have adsorbed thiophene directly on the Pd(111)/S surface. Desorption of thiophene is shown in fig. 2 and occurs up to 480 K. Comparison of the desorption yield from the saturated monolayer indicates that the cyclization reaction

$$2C_2H_2 + S \rightarrow C_4H_4S$$

yields an amount of thiophene corresponding to a coverage of $\sim 2\%-4\%$ of the saturation coverage.

3.2. THIOPHENE PRODUCTION ON THE Pd(111)/S LOW TEMPERATURE PHASE

The thiophene synthesis reaction occurs on the low temperature Pd(111)/S phase but with much lower yield than on the high temperature phase. Prior to the adsorption/desorption experiment the sulfur overlayer was present in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer lattice. Thiophene desorbs in the temperature range 300 K–460 K, similar to that observed on the high temperature phase, but with a total yield $< 1/20$ of that observed on the high temperature phase. Examination of the surface with LEED indicates that the long range order of the sulfur overlayer no longer exists as would be the case after heating without acetylene adsorption.

3.3. THIOPHENE SYNTHESIS FROM $C_4H_4Cl_2$ ON THE Pd(111)/S SURFACE

To obtain mechanistic information about the thiophene synthesis reaction we have followed the lead of Patterson and Lambert [7] in their study of acetylene trimerization to benzene. Cis-3,4-dichlorocyclobutene has been used to produce a surface intermediate with stoichiometry C_4H_4 on both high and low temperature phases of the Pd(111)/S surface. Figure 3 shows the 58, 84, and 122 amu desorption spectra from the Pd(111)/S low temperature phase. The dominant species desorbing from the surface is cis-3,4-dichlorocyclobutene which yields fragments at all three masses. The reaction between the hydrocarbon fragment and the sulfur overlayer leads to thiophene formation and desorption in the temperature range 420 K to 480 K. Figure 4 depicts the results of the same experiment on the high temperature Pd(111)/S phase. Thiophene formation and desorption occur in the same temperature range over this surface however the yield of thiophene is five times that over the low temperature phase. Monitoring of the 122 amu parent ion of cis-3,4-dichlorocyclobutene from both low and high temperature phases indicates that its coverage is identical on both surfaces and that it is the reaction with the adsorbed sulfur that is truly enhanced on the high temperature phase. The effect of chlorine is undetermined. It is present on the surface during the course of the reaction and does not desorb until temperatures of ~ 600 K have been reached. In the acetylene trimerization reaction, chlorine

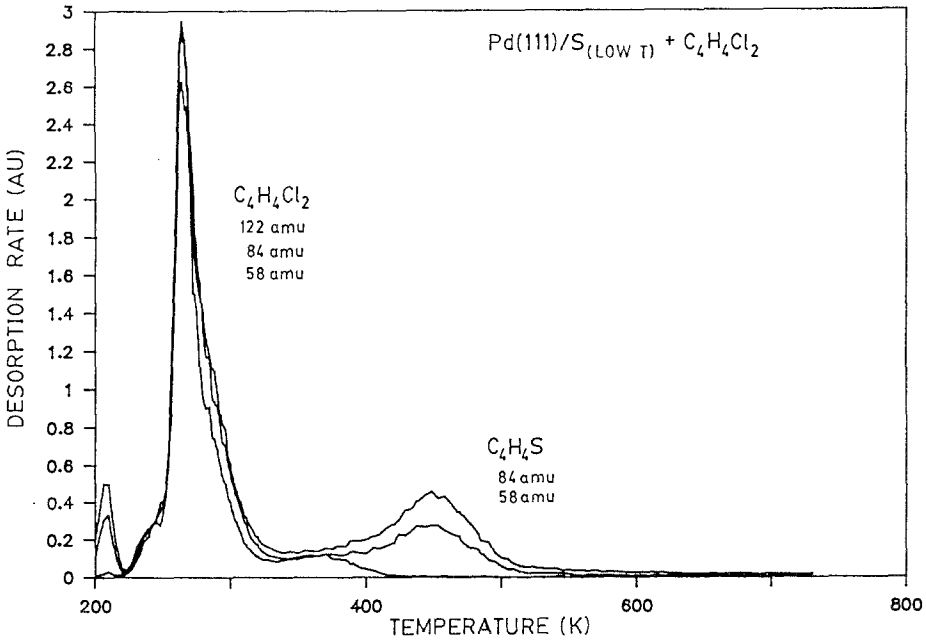

Fig. 3. Thiophene and $C_4H_4Cl_2$ desorption following the adsorption of $C_4H_4Cl_2$ on the low temperature phase of the Pd(111)/S surface.

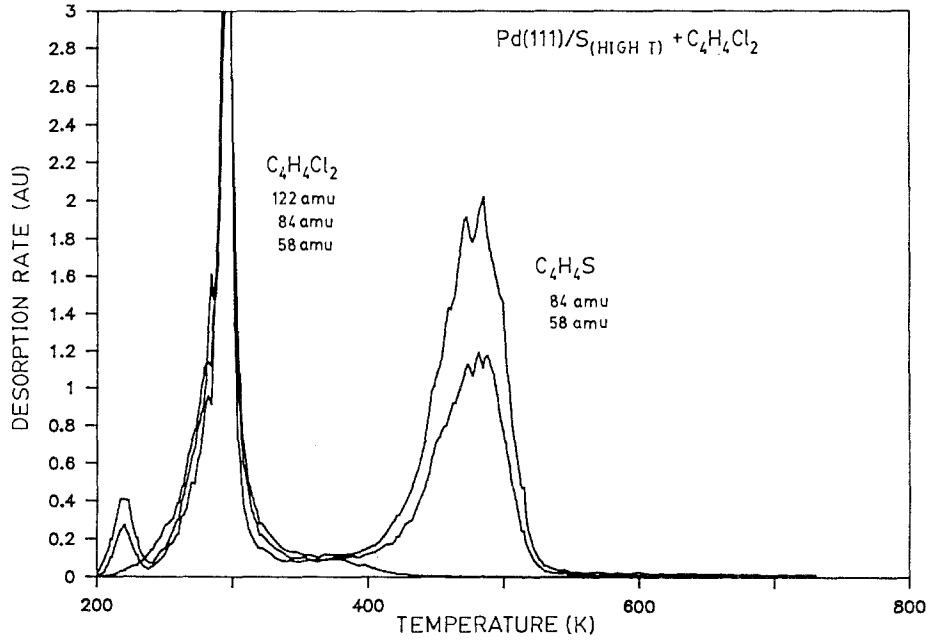

Fig. 4. Thiophene and $C_4H_4Cl_2$ desorption following the adsorption of $C_4H_4Cl_2$ on the high temperature phase of the Pd(111)/S surface.

does not affect the yield of benzene although it does have some effect on the desorption kinetics [4].

4. Discussion

There are a number of interesting aspects to the thiophene synthesis reaction. The fact that it occurs at all is remarkable given the very high heat of adsorption of sulfur on most metal surfaces. Although it is not documented in this letter, it is clear that the formation of thiophene occurs only on surfaces with sulfur coverages approaching saturation. Heating to temperatures of 1100 K is insufficient to induce desorption at a significant rate ($\ll 0.01$ monolayers per sec.), indicating that the sulfur-Pd(111) heat of adsorption is greater than 70 kcal/mole [9].

A second observation that can be made from the examination of the desorption spectra presented in this work is that the upper temperature limit for thiophene desorption is ~ 480 K independent of the route by which it was produced. This is not only the case for thiophene produced from adsorbed acetylene or cis-3,4-dichlorocyclobutene but also for thiophene desorption following low level exposure of thiophene to the sulfided surface. It is apparent that in this temperature range (~ 480 K) it is the same process that is rate limiting in all three cases:

$$2C_2H_2 + S \rightarrow C_4H_4S_{(g)}$$

$$C_4H_4 + S \rightarrow C_4H_4S_{(g)}$$

$$C_4H_4S_{(ad)} \rightarrow C_4H_4S_{(g)}$$

Barring the possibility that thiophene adsorbs dissociatively at low temperatures only to recombine and desorb irreversibly up to 480 K, it appears that thiophene desorption from the surface is the rate limiting process and that thiophene formation occurs at < 480 K.

Finally, the difference in activity between the two phases of the sulfided Pd(111) surface is quite intriguing. The fact that the reaction of adsorbed sulfur with cis-3,4-dichlorocyclobutene yields thiophene desorption at ~ 480 K on both phases indicates that although sulfur atom incorporation into the ring occurs with greater facility on the high temperature phase than on the low temperature phase it is not rate limiting in the process. In this case monitoring the parent ion signal of the desorbing cis-3,4-dichlorocyclobutene indicates that the coverage was the same on both surfaces. In the experiments using acetylene it was not possible to determine the coverages because adsorption is predominantly irreversible. It is quite possible that the sticking coefficient of acetylene varies between the two surfaces and that measurements other than desorption are needed to determine the coverages present after adsorption. It is interesting to note, however, that

although very little thiophene is produced on the low temperature phase the kinetics of benzene formation are similar to those observed on the clean Pd(111) surface. Apparently the reaction which is inhibited on the low temperature phase is the step in which sulfur is extracted from the surface rather than

$$2C_2H_2 \rightarrow C_4H_4$$

On the high temperature phase this reaction occurs with much greater facility. At the same time, however, the formation of benzene is greatly enhanced and the kinetics of its formation and desorption are quite different from those on the low temperature phase.

5. Conclusions

This letter has described the observation of a surface induced reaction in which acetylene and sulfur cyclize to form thiophene. This novel surface chemistry bears some similarity to the observations of cyclization reaction between molecular adsorbates containing triple bonds with the exception that this reaction involves incorporation of an adatom to form a five rather than six membered ring. It appears that it is the desorption of thiophene that is rate limiting in the appearance of thiophene in the gas phase.

In addition to reporting the observation of this reaction it is also noted that distinct differences exist between the chemistry observed on the low temperature versus high temperature phases of the Pd(111)/S surface. The ability to tailor the chemical activity of these surfaces by modifying the form of the sulfide layer is quite remarkable and a better understanding of the differences between the two phases would certainly be interesting.

Acknowledgements

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