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Conversion of Acetylene to Benzene over Palladium Single-Crystal Surfaces. 2. The Effect of Additives

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The conversion of acetylene to benzene over palladium single-crystal surfaces ((111), (100), and (110)) modified with submonolayer quantities of silicon, phosphorus, sulfur, chlorine, and potassium has been studied under both ultrahigh vacuum and atmospheric pressure conditions. At atmospheric pressures electron-donating additives enhance the rate of benzene formation and electron-accepting additives reduce the rate. Potassium and silicon reduce the amount of surface carbon that accumulates during the reaction and thereby increase the rate of benzene formation relative to the undoped surface. The general trends of the (111), (100), and (110) faces indicate that at low pressures potassium suppresses, silicon and phosphorus enhance, and sulfur and chlorine leave unchanged the benzene yield. Silicon on the (100) face showed the greatest enhancement in the benzene yield possibly due to surface compound formation.

1.0. Introduction

Additives are widely used in both low-pressure stoichiometric reactions and high-pressure catalytic reactions to alter the product distribution, to raise the yield, or to increase catalyst lifetime. It is not well understood how the additives modify the catalyst surface for these reactions. Two major types of interactions are possible: (1) a geometric effect due to site blocking and (2) an electronic effect due to the donation or depletion of electron density in the near surface region.

The conversion of acetylene to benzene has been shown to occur both in ultrahigh vacuum and at higher pressures on a variety of palladium surfaces with different morphologies (single crystals,[1-9] films,[1] and small metal particles supported on alumina[1]) as well as over many homogeneous catalysts.[10-12] A comparison of the low-pressure and high-pressure reaction on palladium single crystals is described in detail in the previous paper.[1] In this paper we study the effects of silicon, phosphorus, sulfur, chlorine, and potassium on the chemisorptive and catalytic properties of palladium (111), (100), and (110) single-crystal surfaces on the cyclotrimerization of acetylene. The differences in additive behavior in the low-pressure and the high-pressure (1 atm) reactions are compared. The effect of the additives is quantified by catalytic rates of benzene production from acetylene, temperature-programmed desorption (TPD) of hydrogen, acetylene, ethylene, benzene, and carbon monoxide, and by work function measurements.

2.0. Experimental Section

Experiments were carried out in two ultrahigh vacuum (UHV) chambers. . Low-pressure experiments were conducted in a standard UHV chamber with a base pressure of 1×10^{-10} Torr. The chamber was equipped with a four-grid retarding field analyzer and glancing incidence electron gun for Auger electron spectroscopy (AES) and for work function changes as the surface was modified by additives. Changes in the work function were measured by the change in the onset energy of the secondary electron cascade and were reproducible to within ±10%.

The high-pressure experiments were performed in a UHV/high-pressure apparatus designed for combined UHV surface analysis and high-pressure reaction studies[13] using small surface area catalyst samples. This chamber was equipped with four-grid electron optics for low-energy electron diffraction (LEED), a double pass cylindrical mirror analyzer with coaxial electron gun for AES, an Ar^+ sputtering gun for crystal cleaning, a quadrupole mass spectrometer, and a retractable internal isolation cell that constitutes part of a microbatch reactor operating in the pressure range of 10^{-2}–20 atm. The experimental procedure for both the high-pressure and the low-pressure studies are described in detail in the previous paper.[1]

For additive-doping studies, coverages were estimated from the relative Auger sensitivities of the most intense peaks,[14] which is accurate only for low coverages. The relative additive coverage is given as $\theta_A = (h_A S_A)/(h_A S_A + h_S S_S)$, where h_A and h_S are the peak heights of the adsorbate and substrate and S_A and S_S are the Auger sensitivity factors for the adsorbate and substrate. Potassium was deposited under vacuum from a SAES getters mounted 2 cm from the sample. Silicon (Matheson grade SiH_4), phosphorus (Matheson grade PH_3), sulfur (Matheson grade H_2S), and chlorine (Matheson H.P. grade Cl_2) were deposited on the crystal surface at 300 K through a variable rate leak valve. Subsequently, the crystal surface was heated (700 K) to desorb H_2, and the coverage was determined by AES. Additive coverages remained unchanged, as observed with AES during both UHV and high-pressure experiments.

Product formation was followed by gas chromatography. Initial reaction rates were determined graphically from the slopes of product accumulation curves as a function of time over the first 2–3 h of reaction time and were reproducible to within ±10%. Blank experiments performed on Pd covered with graphitic carbon (formed by heating the crystal in a hydrocarbon atmosphere at 750 K) showed only a low level of catalytic activity. For example, at 575 K the activity of the carbon-covered surface was less than 10% of the activity of clean palladium at the lowest reaction temperature (275 K) used in this study.

3.0. Results

The cyclotrimerization of acetylene was observed on adsorbate-modified (111), (100), and (110) single crystals of Pd. These

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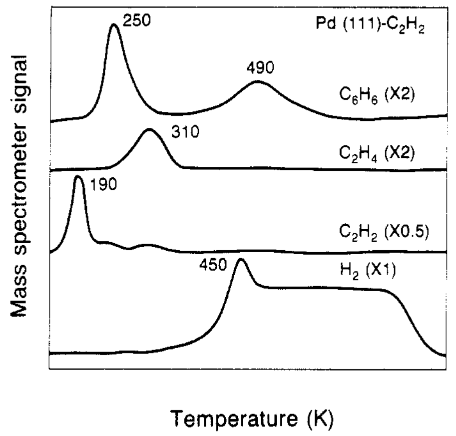

Figure 1. The TPD spectra of acetylene dosed on clean Pd(111) (6 langmuirs of acetylene, 130 K) are displayed. The four desorption products are benzene from cyclotrimerization, ethylene from hydrogenation, acetylene from reversible molecular desorption, and hydrogen from decomposition.

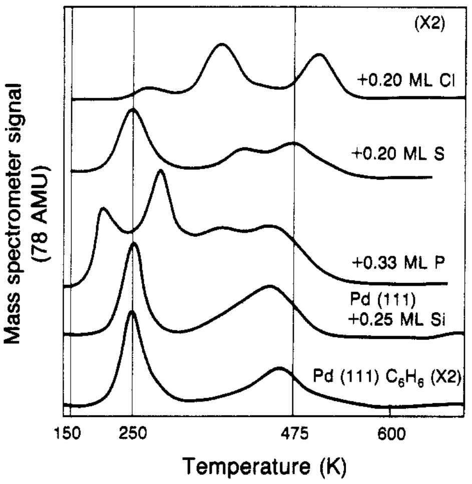

Figure 2. The benzene TPD from 6 langmuirs of acetylene dosed on additive-covered covered Pd(111) at 130 K is displayed. The high-temperature peak shifts to higher temperatures: from 470 K on the silicon-dosed surface to 490 K on the chlorine-covered surface. The phosphorus-covered surface leads to a thermal desorption trace for benzene with four maxima. All spectra magnified by a factor of 2.

surfaces have been studied in ultrahigh vacuum by TPD and at 1 atm pressure by the high-pressure/low-pressure apparatus to obtain kinetic information on the reaction. Detailed information on the trimerization reaction in both pressure regions on clean Pd is reported in the previous paper.[1]

3.1. Effect of Adatoms (Si, P, S, Cl, and K) on the Low-Pressure Stoichiometric Reaction over Palladium Single Crystals. Thermal desorption studies were carried out in UHV for three Pd surfaces ((111), (100), and (110)) to determine the effect of adatoms (Si, P, S, Cl, and K) on the acetylene cyclotrimerization, the decomposition of acetylene to carbon and hydrogen, the self-hydrogenation to ethylene, and the reversible molecular desorption of acetylene. All doses were 6 langmuirs (1 langmuir = 1×10^{-6} Torr s) and at 130 K unless stated otherwise.

3.1.1. Pd(111). As reported previously[1] TPD of 6 langmuirs of acetylene from clean Pd(111) resulted in some reversible molecular desorption at low temperatures (190 K), self-hydrogenation to form ethylene (300 K), decomposition to form hydrogen (430–830 K), and formation of benzene (250–490 K) (Figure 1).

Adsorption of silicon ($\theta = 0.25$) on Pd(111) did not significantly perturb the benzene formation as shown by the thermal desorption results (Figure 2). The only effect of silicon was to slightly decrease acetylene decomposition and enhance the high-temperature desorption peak of benzene. Phosphorus, on the other hand, greatly suppressed the acetylene decomposition, increased the yield of ethylene, and gave rise to a thermal desorption spectrum of benzene (from the cyclotrimerization reaction) with maxima at 200, 300, 400, and 470 K, while doubling the benzene yield (Figure 2).

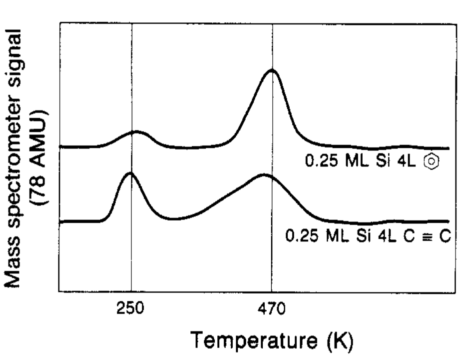

Figure 3. Benzene TPD spectra are compared after dosing silicon-doped Pd(111) with 4 langmuirs of acetylene or benzene at 130 K. Benzene formed from acetylene yields a broader high-temperature peak. Higher acetylene exposures enhance the high-temperature peak, whereas larger benzene exposures increase the low-temperature peak.

Sulfur adatoms also affected the thermal behavior of chemisorbed acetylene (Figure 2). At low sulfur coverages ($\theta < 0.2$), the decomposition to hydrogen and the ethylene yield decreased, while the benzene yield increased significantly. The low-temperature benzene peak intensity almost doubled relative to the clean surface and a new peak appeared at 430 K. At higher sulfur coverages ($\theta < 0.25$), the formation of ethylene was fully suppressed and the decomposition to H_2 was very low. At these high sulfur coverages, the benzene desorption spectrum comprised a broad peak with a single maximum at 260 K equal in intensity to the clean surface.

Like phosphorus and sulfur, chlorine adatoms also enhanced benzene formation (Figure 2). In contrast to sulfur, the benzene desorbed largely in the high-temperature regions, with maxima at 415 and 490 K, although there was a smaller peak at 270 K. Chlorine also suppressed ethylene formation and acetylene decomposition.

The adatoms increased acetylene cyclotrimerization and decreased side reactions in order from silicon to phosphorus to sulfur on Pd(111). Chlorine was not as effective as sulfur, which almost fully suppressed all acetylene reactions except for cyclotrimerization. Thus Pd(111)–S is a selective catalyst for acetylene cyclotrimerization under UHV conditions. The main difference in the TPD spectra between the Pd(111)–S and Pd(111)–Cl surfaces was that the Pd(111)–S surface promoted primarily the low-temperature cyclotrimerization reaction and the Pd(111)–Cl surface promoted the high-temperature process.

TPD studies of adsorbed benzene on adatom-covered palladium surfaces yield similar desorption spectra as benzene formed from acetylene. Figure 3 shows the effect of silicon ($\theta = 0.25$) on Pd(111) on the desorption of benzene and benzene formed from acetylene. Silicon enhanced the high-temperature TPD peak of benzene relative to the clean surface for both acetylene and benzene adsorption. Higher exposures of both acetylene and benzene led to an enhancement of the high-temperature (470 K) benzene desorption peak.

3.1.2. Pd(110). Acetylene chemisorbed on clean Pd(110) resulted in reversible molecular desorption, decomposition, self-hydrogenation, and cyclotrimerization. The yield of benzene from the clean Pd(110) crystal face was found to be approximately one-sixth that of the clean Pd(111) crystal face.

Silicon at low surface coverages ($\theta < 0.25$) enhanced the benzene yield through the high-temperature desorption peak (Figure 4) and decreased acetylene decomposition. At $\theta_{Si} = 0.37$ the yield of benzene increased by a factor of 3.5 (relative to the clean surface), while the ethylene and hydrogen yields were less than that observed for the clean Pd(110) surface. Phosphorus on the (110) surface of palladium increased cyclotrimerization and self-hydrogenation. Benzene desorption was found to increase at phosphorus coverages greater than $\theta = 0.2$. Again, as on

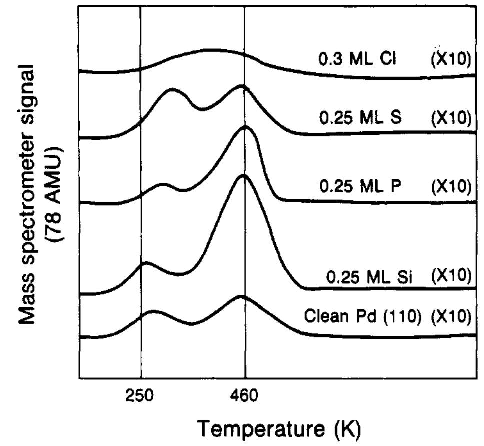

Figure 4. The benzene TPD spectra from additive-covered Pd(110) after a 6-langmuir exposure of acetylene at 130 K are displayed. Silicon and phosphorus increase the high-temperature peak. Sulfur enhances the low-temperature benzene desorption maxima slightly and chlorine reduces the overall yield and broadens the two maxima into one peak.

Pd(111) and Pd(100), the gain in benzene yield was in the high-temperature desorption peak (Figure 4). At higher phosphorus coverages, two benzene TPD maxima were observed at 270 and 440 K. The high-temperature maximum was increased by as much as a factor of 4 ($\theta_P = 0.42$) relative to the clean surface, while the ethylene yield remained at the level of the low coverage surface. The amount of hydrogen desorption decreased.

The benzene yield increased slightly, the ethylene yield decreased, and the molecular desorption of acetylene increased with increasing amounts of sulfur on the surface. At higher sulfur coverages ($\theta_S = 0.4$) no ethylene was detected, very little hydrogen desorbed, and the amount of benzene formed was approximately the same as on the clean Pd(110).

Addition of chlorine to Pd(110) decreased decomposition, hydrogenation, and cyclotrimerization of acetylene. At a chlorine coverage of $\theta = 0.30$, a very weak ethylene desorption peak was observed at 290 K and a broad benzene desorption maximum was observed at 370 K (Figure 4).

3.1.3. Pd(100). A TPD experiment after acetylene adsorption on clean Pd(100) yielded reversible molecular desorption, decomposition, hydrogenation, and cyclotrimerization (Figure 5A–D). The yield of benzene from the clean Pd(100) crystal face was one-twentieth that of the clean Pd(111) crystal face.

Potassium on the (100) face of palladium inhibited benzene formation (Figure 5A). The yield of ethylene and hydrogen decreased by 95% (Figure 5, B and D), and the molecular desorption of acetylene was slightly reduced (20–25%) (Figure 5C). At $\theta = 0.25$ (or higher) coverages of potassium, no benzene formation was observed.

Silicon on Pd(100) substantially enhanced benzene and ethylene formation (Figure 5, A and B). The two benzene TPD peaks were similarly affected by silicon promotion on Pd(100) and Pd(111); that is, the high temperature peak increased and accounted for a sixfold increase in the yield of benzene at a silicon coverage of $\theta = 0.10$. Higher coverages of silicon on Pd(100) ($\theta = 0.38$) further increased the yield of benzene up to 20 times that of the clean surface (Figure 6). The ethylene yield was also enhanced by factor of 10. The decomposition reaction increased as well, although the hydrogen desorption remained constant.

Phosphorus adsorbed on Pd(100) influenced the chemistry of chemisorbed acetylene. The yield of benzene was enhanced, but not to the extent observed on silicon-covered Pd(100). At a phosphorus coverage of $\theta = 0.17$, two benzene maxima were observed, at 350 and 520 K. Low coverages ($\theta < 0.2$) did not change the benzene or ethylene yields. At coverages of $0.3 < \theta_P < 0.5$, the amount of both benzene and ethylene increased by a factor of 3 to 5 (Figure 5, A and B). With increasing phosphorus coverages the benzene desorption maxima were also observed to shift to higher temperatures, primarily to the high-temperature desorption peak at 480 K.

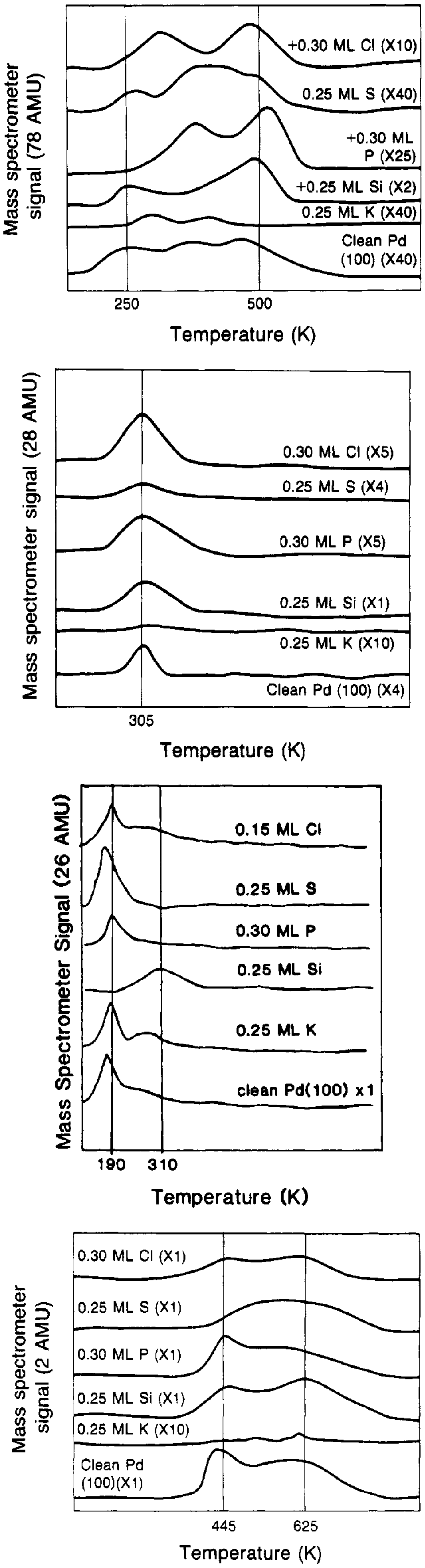

Figure 5. Parts A–D (from top to bottom) present the desorption traces for benzene, ethylene, acetylene, and hydrogen from additive-covered Pd(100) dosed with 6 langmuirs of acetylene at 130 K. Note the scaling factors. The benzene desorption changes both in the desorption temperature and desorption yield. Potassium suppresses desorption of all products except for acetylene. Silicon-covered Pd(100) produces 15 times more benzene than the clean surface.

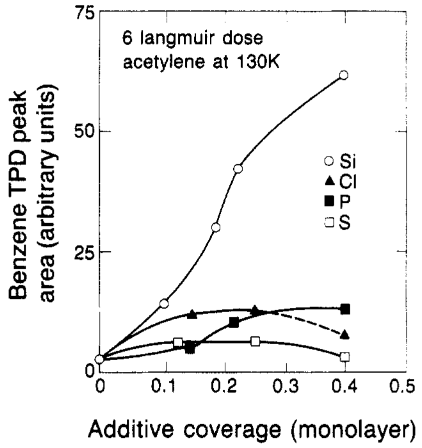

Figure 6. The benzene TPD peak area on Pd(100) is shown as a function of additive coverage after dosing with 6 langmuirs of acetylene at 130 K. Electron-withdrawing additives, sulfur and chlorine, and electron-neutral phosphorus alter benzene formation to the same extent: initially increasing benzene formation and then for coverages greater than $\theta = 0.22$ decreasing benzene formation. Silicon enhances benzene formation to $\theta = 0.38$ (highest coverage studied) at which point 20 times more benzene forms than on the clean surface.

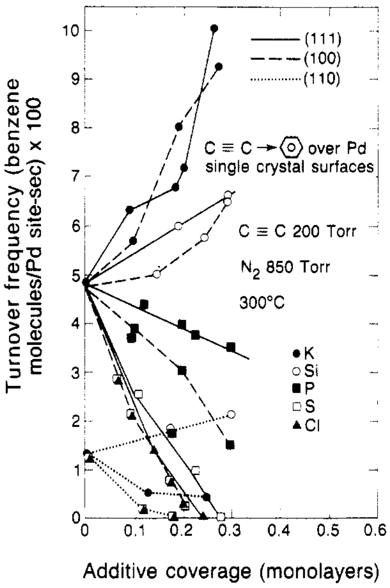

Figure 7. The effect of additives on the catalytic rate of benzene formation at atmospheric pressures on the Pd(111), Pd(100), and Pd(110) surfaces is shown. The additives have the same effect on Pd(111) and Pd(100). Potassium and silicon enhance the rate and phosphorus, sulfur and chlorine decrease the rate of benzene formation. On the Pd(110) surface, which has a lower rate on the clean surface, silicon and phosphorus enhance the rate of benzene formation whereas sulfur, chlorine, and potassium decrease the rate.

Low sulfur coverages on Pd(100) ($\theta_S < 0.25$) decreased the yield of ethylene (Figure 5B) and only slightly increased the benzene yield (Figure 5A). The desorption of hydrogen decreased markedly for all sulfur coverages, and the desorption spectra was very broad, ranging from 435–610 K (Figure 5D). The major change observed at higher sulfur coverages was the decrease in ethylene yield. For example, at $\theta_S = 0.25$ the ethylene yield was one-half that of the clean surface (Figure 5B).

Chlorine was found to enhance the yield of both ethylene and benzene (Figure 5, A and B). The effect was much smaller than that observed for either silicon of phosphorus. For coverages of $\theta_{Cl} = 0.3$ the yield of benzene was 5 times higher than for the clean surface.

The additive coverage dependence of benzene formation was studied on the Pd(100) surface (Figure 6). Sulfur and chlorine enhanced benzene formation up to coverages of $\theta = 0.25$ and at higher coverages hindered benzene formation. Silicon and phosphorus increase benzene production to the highest coverages studied ($\theta = 0.4$).

3.2. Effect of Adatoms (K, Si, P, S, and Cl) on the High-Pressure Catalytic Reaction on Palladium Single Crystals. High-pressure catalytic studies were carried out over three palladium surfaces ((111), (100), and (110)) to determine the effect of adatoms on the acetylene cyclotrimerization. Reactions were carried out between 290 and 620 K at an acetylene pressure of 200 Torr. Reaction rates were calculated by assuming that each palladium surface atom was one reaction site, and no correction was made when adatoms were deposited on the surface. This leads us to report conservative values for the reaction rates. All reactions produced benzene and very small amounts of C_4 hydrocarbons. Small amounts of ethylene (<5% of the benzene formed) were not detectable by gas chromatography due to the large acetylene reactant gas peak tail.

3.2.1. Pd(111) and Pd(100). The initial rate of benzene production on clean Pd(111) and Pd(100) at 573 K with 200 Torr of acetylene was found to be 0.05 molecule of benzene produced per palladium surface atom per second.[1] Potassium had the greatest positive effect on the rate of benzene production on Pd(111) (Figure 7). With $\theta_K = 0.25$ of potassium (200 Torr of acetylene, 850 Torr of nitrogen, 570 K) the rate doubled to 0.10 molecule/(site·s). When potassium was present on the surface, less graphitic carbon appeared in AES (due to the decomposition reaction) and the rate of poisoning was reduced relative to the clean surface. Silicon also accelerated the rate of benzene formation. For example, at a coverage of $\theta_{Si} = 0.33$ the rate increased by 35%. Similarly, relative to the reaction over clean Pd(111), the amount of graphitic carbon deposition was reduced with silicon present on the surface. The amount of graphitic carbon on the surface after the reaction was determined by CO titration, as described in the previous paper.[1]

Phosphorus depressed the reaction rate (Figure 7). At $\theta_P = 0.33$ the rate of benzene production was reduced by 37%. The graphitic carbon deposition rate and the poisoning rate were similar to that of clean Pd(111).

Sulfur and chlorine greatly depressed the reaction rate. For coverages greater than $\theta = 0.20$, no benzene formed. Reactions on chlorinated surfaces were carried out at room temperature due to the low desorption temperature of chlorine from palladium surfaces under reaction conditions. The facile desorption of chlorine under reaction conditions (300 K, 250 Torr of acetylene, 850 Torr of nitrogen) is in sharp contrast to the reported desorption temperature in UHV of 950 K.[15] The rate of benzene formation on chlorine covered surfaces was very low, even for coverages as low $\theta = 0.1$. For coverages over $\theta = 0.2$ no benzene was observed.

The activation energy and pressure dependence for benzene formation on additive covered surfaces did not change from the values obtained on the clean surface (activation energy = 2.1 kcal mol^{-1}, rate = $kP_{C_2H_2}$).[1]

3.2.2. Pd(110). The rate of benzene formation on clean Pd(110) was found to be one-fourth that of Pd(111) under the same reaction conditions.[1] Additives had less effect on the (110) surface than on the (111) and (100) surfaces. In contrast with potassium doping of the (111) and (100) surfaces, adsorption of potassium on the (110) surface decreased the rate of benzene formation (Figure 7). Silicon and phosphorus both enhanced the rate of benzene formation to the same extent. As on Pd(111) and Pd(100), sulfur and chlorine depressed the reaction rate on the (110) surface.

4.0. Discussion

The cyclotrimerization reaction of acetylene on clean Pd catalysts proceeds readily in pressures ranging from 1×10^{-12} to 1 atm and on a variety of surfaces (single crystals, films, and alumina supported).[1] The reaction is structure sensitive at both low and high pressure. In UHV the stoichiometric reaction over the (111) face is the most active. The (110) face is one-sixth as active, and the (100) surface is one-twentieth as active as the (111) face. At high pressure the (111) and (100) surfaces show similar catalytic rates and the (110) face is one-fourth as active. In addition to

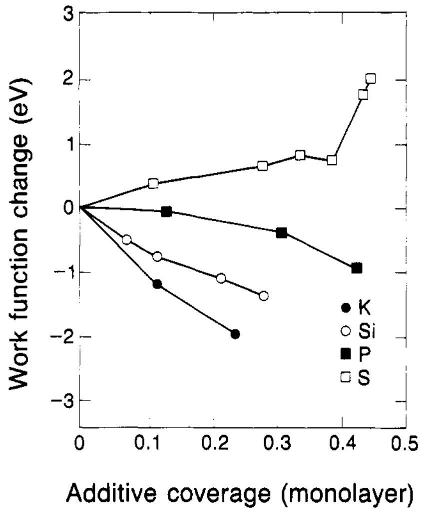

Figure 8. The change in work function is plotted vs. the additive coverage on the Pd(100) surface. Sulfur withdraws electron density from the surface whereas potassium, silicon, and phosphorus donate electron density to the surface.

the cyclotrimerization reaction, hydrogenation, reversible molecular desorption, and decomposition reactions are detected at low pressure and decomposition/polymerization is detected at high pressure. At high pressure the reaction has an apparent activation energy of 2.1 kcal mol^{-1} and is first order in acetylene pressure (rate = $kP_{C_2H_2}$).

This study investigates the effect of additives (K, Si, P, S, and Cl) on the cyclotrimerization of acetylene over palladium single crystals ((111), (110), and (100)) at both low and atmospheric pressures. The difference in benzene yield at low pressures (relative to the differences in rate of benzene production at high pressures) over the different modified surfaces was quite dramatic. Potassium was found to virtually eliminate all benzene formation at low pressures, whereas at high pressures, in general, it was found to be the best promoter for the catalytic formation of benzene. Sulfur and chlorine, on the other hand, slightly enhanced the low-pressure formation of benzene, while at higher pressures even very low coverages ($\theta < 0.1$) of sulfur or chlorine poisoned the reaction, and above $\theta = 0.25$ no benzene formation was observed. The effects of the different additives will be discussed in terms of steric (site blocking) and electronic (electron-donating or -withdrawing) interactions with the surface. The high-pressure catalytic and the low-pressure stoichiometric results will also be compared.

To observe how the surface electronegativity changes with the addition of different adatoms to the surface, we performed work function measurements on Pd(100) (Figure 8). The change in work function varies linearly with the coverage of each additive. The decrease in work function is greatest for potassium, indicating that it donates the most electron density to the surface per unit coverage, followed by silicon and then phosphorus. Conversely, sulfur increases the work function, implying that it withdraws electron density from the surface. These trends correspond to previous work function trends reported for the Cl/Pd and K/Fe systems.[15,25] The work function changes observed correlate to the differences in Pauling electronegativities between the additives and palladium. Potassium (0.82) and silicon (1.9), which are more electropositive than Pd (2.2), donate electron density to the surface and decrease the work function. Sulfur (2.6) which is more electronegative withdraws electron density and increases the work function. Phosphorus (2.19) is essentially electroneutral with palladium, but work function measurements show that it decreases the work function.

Both acetylene and benzene are known to donate electrons to metal surfaces.[16-18] Acetylene has a low-lying antibonding orbital

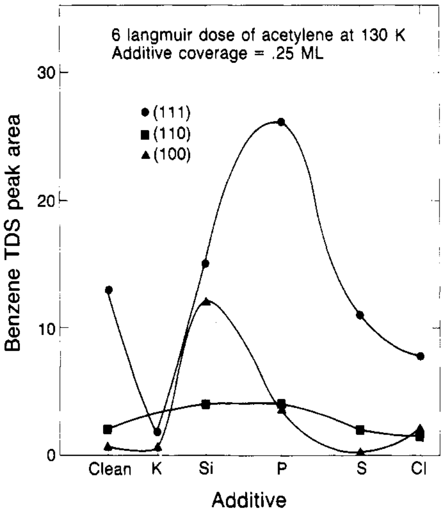

Figure 9. This figure compares the effect of $\theta = 0.25$ of additives on the benzene yield at low pressures on Pd(111), Pd(110), and Pd(100). Benzene TPD spectra were recorded after a 6-langmuir dose of acetylene at 130 K. Phosphorus on Pd(111) and silicon on Pd(100) increase benzene formation the most.

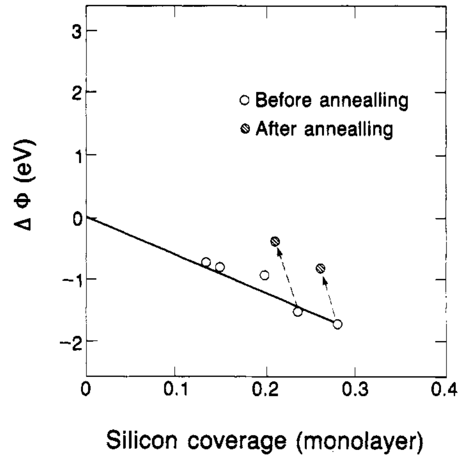

Figure 10. The change in work function is plotted as a function of silicon coverage on Pd(100). After the crystal was annealed at 770 K for 4 min the work function shifts 0.75–1.25 eV, while the silicon coverage, as detected by AES, remains almost constant.

which is partially filled in the presence of electron donors on the metal surface, such as potassium, which destablize the carbon–carbon bond.[17] Benzene's antibonding orbitals have lower binding energies and are not filled even in the presence of potassium as evidenced by the TPD and electron energy loss spectroscopy of this group.[19,20]

Studies have found potassium to be uniformly dispersed on metal surfaces[21,22] (except at multilayer coverages), whereas sulfur and chlorine form ordered islands at low coverages.[23] Phosphorus and silicon form ordered LEED structures over some Pd surfaces.[24] For example, on Pd(111), phosphorus formed a ($\sqrt{7} \times \sqrt{7}$)*R17°* pattern.

4.1. Low-Pressure Studies. The UHV results are summarized in Figure 9, which shows the effect of $\theta = 0.25$ of additive on the

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benzene yield. The most pronounced effect was that of silicon on the Pd(100) surface, where, at a coverage of $\theta_{Si} = 0.38$, the yield of benzene increased twentyfold. Phosphorus on the (100) surface increased the benzene yield approximately twelvefold. The enhanced amount of benzene over these two surfaces may be attributed to the formation of surface compounds. Changes in the work function after annealing (770 K) for silicon on the Pd(100) surface support this claim (Figure 10). For a silicon coverage of $\theta = 0.27$, the work function increases approximately 0.75 eV, approaching the value of the clean palladium surface. This increase corresponds to silicon dissolution in the surface region, as shown by the slight change of the AES silicon signal (no silicon desorption was observed). This work function change has been shown to indicate surface compound formation.[25-32] PdSi is known to be a stable compound.[33] These changes in the work function were not observed for any of the other additives on the Pd(100) surface.

Potassium is the least likely of the additives studied to form islands on the metal surfaces and only at coverages approaching saturation do LEED patterns form.[23] Less initial reaction sites would be available for a potassium-doped surface than would be for a silicon-, phosphorus-, sulfur-, or chlorine-modified surface which form islands at low coverages. The negligible conversion of acetylene to benzene is possibly due to potassium-blocking sites. With dispersed potassium on the surface, three acetylene molecules would be less likely to be close enough together on the surface to form benzene.

Sulfur suppressed the decomposition reaction. Relative to the three clean surfaces, only 5–10% as much H_2 and ethylene were observed in the TPD experiments. Anderson and co-workers[16,17] predicted that electron-withdrawing additives would block most acetylene adsorption and weaken the acetylene—metal bond. The weakened acetylene–palladium surface bond accounts for the large decrease in the amount of decomposition. Benzene formation remained approximately unchanged and molecular desorption was slightly enhanced.

Chlorine also reduced the amount of acetylene decomposition, but not to the same extent as sulfur. Molecular desorption of acetylene was enhanced. Benzene formation was enhanced slightly on Pd(100) while it declined slightly on Pd(111) and Pd(110). Chlorine should act very much like sulfur, because both additives withdraw electron density from the surface and form ordered structures at low coverages indicating island formation. It is interesting that for similar coverages of sulfur and chlorine that 2–10 times more hydrogen evolves from the chlorinated surface.

In general, the trend from $K \rightarrow Si \rightarrow P \rightarrow S \rightarrow Cl$ seems to indicate that increasingly electron-withdrawing additives lead to decreasing decomposition and increased benzene yields relative to the clean surface. The most electron-withdrawing additive, chlorine, breaks this trend. The site blocking contribution to the surface reaction appears to be greatest for potassium and decreases as the additive becomes more electronegative.

4.2. High-Pressure Studies. The effect of additives (K, Si, P, S, and Cl) at atmospheric pressures on the reaction of acetylene over single crystals of palladium has been investigated. The additives had the same effect on the Pd(111) and Pd(100) surfaces. The electron-donating additives enhanced the rate of benzene formation (Figure 7). Potassium and silicon, which donated the most electron density to the surface as determined by the change in work function, increased the reaction rate by a factor of 2 and 1.3, respectively, at a coverage of $\theta = 0.3$. Electron-withdrawing additives (S, Cl) decreased the rate of benzene formation and also increased the amount of carbon present on the surface after the reaction. The activation energy and pressure dependence for the formation of benzene did not change from the clean surface for all the modified surfaces studied.

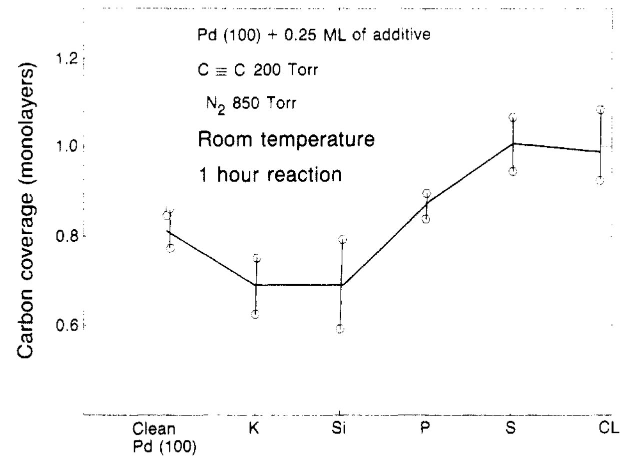

Figure 11. The effect of additives on the final carbon coverage Pd(100) is shown here. Electron-donating additives (potassium, silicon) limit carbon buildup on the surface relative to the undoped surface. Electron-withdrawing additives have higher carbon levels and faster rates of poisoning relative to the undoped surface. Carbon coverage measured after 3 h of reaction time.

The difference in the rate of benzene formation for the different modified surfaces is related to the amount of open Pd surface area. During the reaction, carbon deposited on the surface blocks reaction sites. This surface carbon could be in the form of graphite or a polymer with CH or C_2H stoichiometry.[9] Electron-withdrawing additives enhance the polymerization process, by acidifying the metal surface.[34] The increased surface carbon coverage decreases the rate of benzene formation. Figure 11 shows the amount of carbon present on the (100) surface after 3 h of a high-pressure reaction at room temperature, as detected by AES and CO titrations after flashing the modified surface to 520 K in UHV. Electron-donating additives keep the surface cleaner by slowing the surface polymerization reaction. At high pressures the additives shift the product distribution of the acetylene reaction between benzene and surface polyacetylene or decomposition.

Phosphorus does not fit the trend of electron donors acting to enhance the rate of benzene formation. It appears to have slightly more carbon at equilibrium than the clean Pd(100) surface. The donating power of phosphorus is insufficient to stop either polymerization or decomposition.

The clean Pd(110) surface has only approximately 2% clean surface at steady-state reaction conditions, which is used to explain the lower rate of benzene production relative to the other surfaces. The (110) surface of fcc metals can be thought of as a monotonically stepped surface. This high density of steps is expected to increase decomposition of acetylene and lead to high surface carbon coverage.

The additives on Pd(110) had less effect on the rate of benzene formation than on the (111) and (100) surfaces. Surprisingly, potassium inhibited benzene formation whereas phosphorus enhanced the rate as much as silicon. The interaction of potassium on this surface is not well understood.

5.0. Conclusions

Our results for additive effects on the conversion of acetylene to benzene over palladium single crystals are quite different at high and low pressures. The high-pressure catalytic results appear to depend on the amount of bare palladium exposed. At high pressures the surface is saturated with acetylene and the formation of benzene competes with the decomposition and polymerization

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reactions which poison the catalytic sites. Additives which keep the surface cleaner, such as potassium and silicon, enhance the rate of benzene formation. Sulfur and chlorine appear to enhance the polymerization or decomposition reactions which poison the catalytically active sites. The low-pressure stoichiometric reaction that yields benzene from acetylene is inhibited by site blocking for electron-donating additives and enhanced due to electronic interactions for electron-accepting additives.

From these results it is evident that the effect of the additives on the acetylene cyclotrimerization varies considerably between low pressure and atmospheric pressure. They exhibit both site blocking and electronic interactions that markedly change the benzene yield.

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Registry No. $HC\equiv CH$, 74-86-2; $H_2C=CH_2$, 74-85-1; C_6H_6, 71-43-2; Pd(111), 7440-05-3; Si, 7440-21-3; Cl_2, 7782-50-5; P, 7723-14-0; K, 7440-09-7.

ESR Characterization of V_2O_5 Monolayers and Double Layers Supported on Various Carriers

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Monolayers and double layers of V_2O_5 supported on Al_2O_3, SiO_2, and MgO have been investigated by electron spin resonance spectroscopy. The **g** and hyperfine tensors of V^{4+} determined from the spectra are used to estimate the influence of the carriers on the vanadyl bond strength and the delocalization of the 3d electron on the coordinatively bound oxygen ligands. Spectra of V_2O_5 supported on Al_2O_3 and SiO_2 exhibit a large g tensor anisotropy, corresponding to a relatively short V=O bond. Reduction is found to have a different influence on the V=O bond strength in these two systems: On Al_2O_3 the bond is weakened, whereas on SiO_2 the bond strength is increased. On MgO the spectra indicate a weak vanadyl bond which does not change significantly upon reduction. The delocalization of the V^{4+} electron into ligand orbitals is largest for the MgO-supported systems. Reduction results in an increased delocalization on Al_2O_3 and SiO_2 carriers, whereas with MgO no significant change of this parameter is observed.

The deposition of monolayers or double layers of an active phase on a carrier is an attractive technique for the tailoring of catalytic properties. It offers the advantage of a uniform distribution of active sites and allows one to influence the properties of the active phase by its interaction with the support. This approach has recently been applied for the immobilization of V_2O_5 on Al_2O_3, SiO_2, MgO, and TiO_2.[1] The preparation starting with vanadyl triisobutoxide, the textural properties of the resulting catalysts, and the carrier influence on the reducibility of the V^{5+} ions have been investigated.[1] Of particular interest was the bifunctional activity of these catalysts for dehydration and selective oxidation of alcohols to the corresponding aldehydes. The oxidative activity could be tailored by the acidity of the carrier and the deposition of V_2O_5 species. Catalytic activity has been tested for methanol and 1-heptanol oxidation.

The vanadyl bond strength, as qualitatively derived from temperature-programmed reduction (TPR), was found to parallel the selectivity of methanol oxidation to formaldehyde. Spectroscopic information on the coordination geometry of the supported V_2O_5 species is desired as a more quantitative measure of the V=O bond strength. ESR spectroscopy has been used to provide this information from an analysis of the **g** and hyperfine tensors of $^{51}V^{4+}$ ions.

ESR measurements have been performed on a conventional Varian Century series X-band spectrometer with 100-kHz modulation at room temperature. The microwave frequency was 9.511 GHz. The signals due to ^{51}V with $I = ^7/_2$ were observed from all the catalysts. Samples were analyzed before and after reduction (TPR) in hydrogen. The spectra could be attributed to V^{4+} ions for all catalyst except one. Some of the observed spectra are presented in Figures 1 and 2.

TABLE I: Parameters Characterizing the ESR Spectra of Monolayer and Double Layer Catalysts

catalyst	$g_\parallel$	$g_\perp$	$\Delta g_\parallel/\Delta g_\perp$	$\lvert A\rvert_\parallel$, G	$\lvert A_\perp\rvert$, G	β_2^{*2}	K_{eff}
Al_2O_3–V^{4+}	1.942	1.974	2.1	191	63	0.75	0.53
after TPR	1.947	1.950	1.1	179	73	0.63	0.53
Al_2O_3–$2V^{4+}$	1.938	1.979	2.8	194	66	0.75	0.55
after TPR	1.946	1.953	1.1	181	78	0.61	0.56
SiO_2–V^{4+}	1.934	1.974	2.4	193	73	0.69	0.57
after TPR	1.930	1.979	3.1	194	71	0.70	0.57
SiO_2–$2V^{4+}$	1.932	1.971	2.3	195	75	0.69	0.58
after TPR	1.930	1.975	2.7	196	70	0.72	0.57
MgO–V^{4+}	1.954	1.965	1.3	174	75	0.59	0.55
after TPR	1.953	1.964	1.3	175	77	0.58	0.55
MgO–$2V^{4+}$	1.953	1.966	1.4	172	77	0.56	0.55
after TPR, V^{2+}	1.981	1.981	1.0	80	80		
after TPR, V^{4+}	1.946			176			

In the following section the relationships between ESR parameters, coordination geometry, and electron delocalization are summarized. Subsequently, the experimental results are presented and discussed in terms of changes in the V=O bond strength and in electron delocalization over the ligand orbitals.

Analysis of the Spectra

The powder spectra have been reduced by computer simulations including second-order corrections. The envelopes exhibit shoulders at magnetic field positions corresponding to $g_\parallel$, with a multiplet splitting due to the hyperfine coupling tensor component $A_\parallel$. The magnetic field positions corresponding to $g_\perp$, with an

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