On the effect of hydrogen on the palladium-catalyzed formation of benzene from acetylene

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An infrared spectrum of a Pd(111) surface collected in the presence of 5 Torr of acetylene as a function of hydrogen pressure reveals that the ethylidyne coverage increases with hydrogen pressure ($P(H_2)$ between zero and 20 Torr). The amount of CO that can be accommodated onto the surface at a pressure of 5 Torr, measured after evacuating the acetylene and hydrogen, increases linearly with hydrogen pressure, and this effect is ascribed to the presence of a more open surface produced by the formation of ethylidyne. It is found that acetylene adsorbs in ultrahigh vacuum on ethylidyne-covered Pd(111) and reacts to form benzene, where the benzene desorbs at ∼280 K. This effect is mirrored in the catalytic chemistry where the rate of benzene formation from acetylene in the presence of hydrogen increases linearly with hydrogen pressure.

KEY WORDS: acetylene cyclotrimerization; Pd(111) model catalyst; effect of hydrogen; reflection–absorption infrared spectroscopy; temperature-programmed desorption spectroscopy; catalytic reactions

1. Introduction

Palladium-catalyzed formation of benzene from acetylene has been extensively studied over the past twenty years [1,2]. This is a particularly attractive reaction for fundamental studies since it proceeds both under ultrahigh vacuum conditions [3] as well as at high pressures [4,5]. Work on probing the reaction in ultrahigh vacuum on clean Pd(111) has shown that benzene is rapidly formed from acetylene following adsorption at ∼100 K via reaction of a C_4H_4 metallacyclic intermediate with adsorbed C_2H_2 [6], and desorbs in two states at ∼280 and 520 K with a small peak detected at ∼380 K. These are desorption-rate-limited states, where the low-temperature (∼280 K) feature is assigned to the desorption of tilted benzene desorbing from a crowded surface, and the 380 and 520 K states to the desorption of flat-lying benzene [7]. The surface "crowding" can also be simulated by co-adsorbing acetylene with NO [8]. More recently the presence of the tilted and flat-lying species has been confirmed using high-resolution X-ray photoelectron spectroscopy [9]. Under catalytic conditions, however, the Pd(111) surface is covered by a vinylidene monolayer ($\Theta_{\text{vinylidene}} = 1.0$ [3]). It has been shown that CO can still access the palladium surface, in spite of the presence of this crowded carbonaceous layer, where the CO saturates at a coverage of ∼0.15 monolayers at a pressure of 5 Torr [10]. It has been demonstrated that the presence of the vinylidene overlayer modifies the surface reaction pathway so that benzene is formed under catalytic conditions via an initial reaction between acetylene adsorbed at high pressures onto the palladium surface, and vinylidene species [11], indicating that vinylidenes are not inert spectator species. It has also been found that, both on high-surface-area, supported palladium catalysts [12], and on planar model systems [13], the addition of hydrogen to the acetylene, in addition to forming ethylene, enhances the rate of benzene formation. It has also recently been shown that an adsorbed vinylidene overlayer converts into ethylidyne species in the presence of high pressures (∼0.5 Torr) of hydrogen [14]. Furthermore, CO adsorbs much more easily on ethylidyne-covered Pd(111) than on the vinylidene-covered surface [15]; in the latter case, CO pressures of ∼5 Torr are required to saturate the surface with CO at 300 K, while in the former case, three-fold hollow sites are occupied when exposed to 2 L of CO, and atop sites are all occupied at a CO pressure of $\sim 10^{-2}$ Torr [15]. This suggests that a possible reason for the enhanced rate of benzene formation when the surface is exposed to a $C_2H_2 + H_2$ mixture is that hydrogen reacts with adsorbed vinylidene species forming a more open ethylidyne-covered surface. This suggestion is tested in the following by monitoring the nature of the catalytic surface during reaction using infrared spectroscopy. The openness of the surface is probed, after reactions on a Pd(111) single crystal, using CO chemisorption. This is compared to the rate of benzene formation where a good correlation is found between the two measurements.

2. Experimental

Several pieces of apparatus were used for these experiments which have been described in detail elsewhere [10,16,17]. The first is a high-pressure catalytic reactor enclosed in an ultrahigh-vacuum chamber [16]. The reactor is a coaxial, high-pressure cell which can be sealed and

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filled to 1 atm while maintaining ultrahigh vacuum (~2 × 10^{-10} Torr) in the rest of the apparatus.

Infrared spectra were collected in a chamber that has been described in detail previously [17]. The sample is enclosed in a small volume cell which can be pressurized to 760 Torr to allow surface infrared spectra to be collected under high-pressure conditions.

The third chamber is a molecular-beam chamber [10] which can also be used to collect temperature-programmed desorption data.

The acetylene used for these experiments (Linde, Purified Grade) was transferred from the cylinder to a glass bottle and further purified by repeated bulb-to-bulb distillations and its cleanliness either monitored mass spectroscopically or by using a gas chromatograph. The hydrogen (Aldrich, CP Grade) was used directly from the cylinder and the CO (Linde, Research Grade) was transferred to a glass bottle. This was dosed while a cold finger was immersed in liquid nitrogen to prevent possibly less volatile contaminants (e.g., carbonyls) from entering the system.

3. Results

Figure 1(a) plots the ethylidyne coverage on a Pd(111) surface as a function of hydrogen pressure in the presence of 5 Torr of acetylene at 300 K. The ethylidyne coverage was measured from the integrated intensity of the relatively intense 1327 cm^{-1} methyl bending mode of the ethylidyne species [17]. This assumes that the integrated absorbance of this feature is proportional to coverage. At the relatively low coverages measured here, this should be a reasonable approximation. The absolute ethylidyne coverage was calibrated from the integrated absorbance of a saturated ethylidyne overlayer ($\Theta_{sat} = 0.25$, where coverages are referenced to the number of exposed palladium atoms on the (111) surface [15]). These spectra were collected using exactly identical conditions. The CH_2 mode of adsorbed vinylidene is much less intense and could not be used for quantitative coverage measurements with the sensitivity of the apparatus used for these experiments. In the absence of hydrogen ($P(H_2) = 0$), the surface consists entirely of vinylidene species [3] and, as the hydrogen pressure increases, the relative ethylidyne coverage increases, apparently up to a maximum of ~0.07 ± 0.01 monolayers. This corresponds to a ~1/3 of the saturation ethylidyne coverage of 0.25 monolayers [15]. Following each of these experiments, the reaction cell was evacuated to ~1 × 10^{-9} Torr and pressurized with 5 Torr of CO. The amount of CO adsorbing onto the surface was monitored from the integrated intensity of the CO feature at 1850 cm^{-1}, where this frequency is independent of coverage [10], and confirms that the CO is adsorbed onto the palladium surface. A CO pressure of 5 Torr was selected since CO saturates at this pressure on a vinylidene-covered surface [10]. The amount of CO adsorbed on the surface following reaction with various pressures of hydrogen, and 5 Torr of acetylene, is plotted in figure 1(b). Assuming that the CO coverage varies linearly with the integrated absorbance of the CO signal, these data also represent the CO coverage versus hydrogen pressure. Note that the strong dipole–dipole coupling between adsorbed CO molecules can cause non-linearities in plots of absorbance versus coverage at high coverages. However, the presence of a carbonaceous overlayer that isolates CO molecules from each other is likely to minimize this effect. In addition, the observation that the CO vibrational frequency does not change with coverage suggests that the coupling is small. These data reveal that the amount of CO that can be accommodated onto the surface increases linearly with hydrogen pressure.

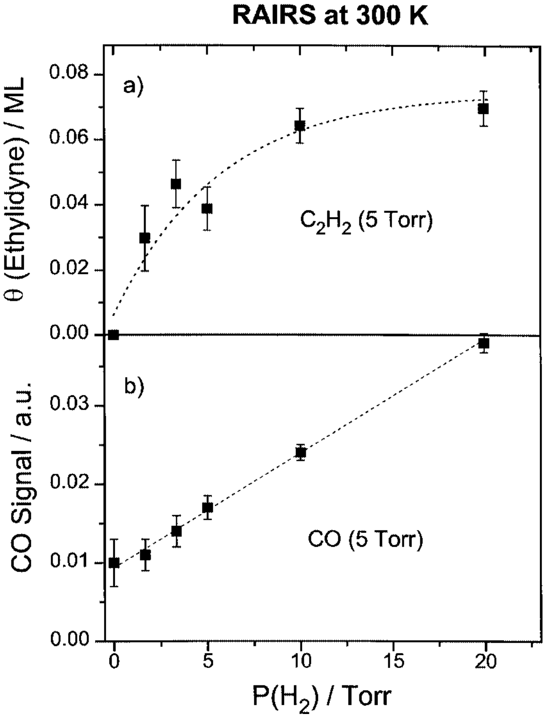

Figure 1. (a) The ethylidyne coverage measured using infrared spectroscopy for the reaction of acetylene and hydrogen on Pd(111), where the acetylene pressure is 5 Torr, plotted versus hydrogen pressure; (b) plot of the integrated CO absorbance under a pressure of 5 Torr of CO following reaction between acetylene and hydrogen on Pd(111) as a function of hydrogen pressure.

Figure 2 shows the effect of an ethylidyne overlayer on the chemistry of acetylene on Pd(111). For comparison, figure 2 (a) and (c) display the 2 (H_2) and 78 (C_6H_6) amu temperature-programmed desorption spectra after acetylene adsorption (5 L) on clean Pd(111), and reproduce previous data [3]. Hydrogen evolves in a broad feature between 450 and 750 K with a peak at ~480 K due to the thermal decomposition of vinylidene species formed on the surface. Benzene desorbs predominantly in two features at 280 and 520 K with a small peak at ~380 K. These have previously been assigned to the desorption of tilted benzene at 280 K and flat-lying benzene at 380 and 520 K [7]. The corresponding 2 (H_2) and 78 (C_6H_6) amu spectra, following acetylene adsorption on an ethylidyne-covered surface, are shown in figure 2 (b) and (d). The broad vinylidene-decomposition feature is still present at between 450 and 750 K indicating

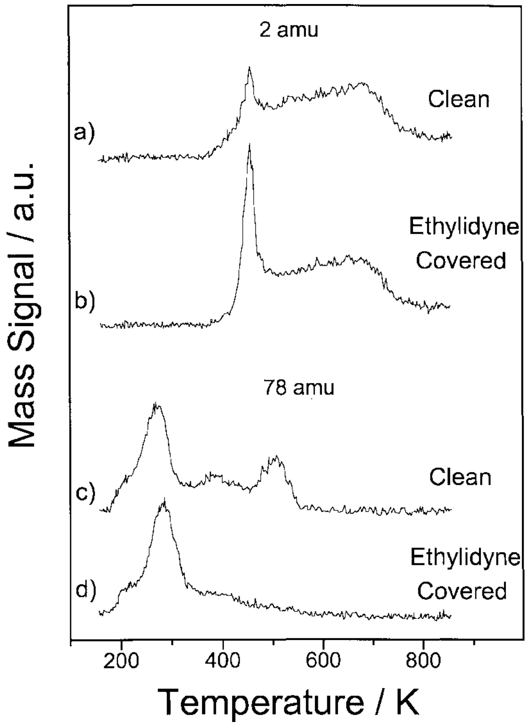

Figure 2. 2 amu temperature-programmed desorption spectra for (a) acetylene (5 L) adsorbed on clean Pd(111) and (b) on an ethylidyne-saturated surface ($\Theta_{\text{ethylidyne}} = 0.25$) and the corresponding 78 amu spectra for (c) acetylene (5 L) adsorbed on clean Pd(111) and (d) on ethylidyne-covered Pd(111).

that vinylidene species are also formed on the ethylidyne-covered surface. The increased 2 amu intensity at ~480 K is due to the thermal decomposition of ethylidyne species. This temperature is slightly higher than for ethylidyne decomposition on clean Pd(111) (~450 K) suggesting that ethylidyne decomposition is inhibited by the presence of vinylidene species. A similar effect has been noted for ethylidyne species co-adsorbed with CO [15]. The corresponding benzene (78 amu, figure 2(d)) spectrum shows a single peak at ~290 K. This is slightly higher in temperature, but close to, the low-temperature feature for acetylene on clean Pd(111) (figure 2(c)). This shows that benzene is still formed in ultrahigh vacuum on an ethylidyne-covered surface and that the surface crowding due to the presence of ethylidyne species causes the benzene to tilt [8], and completely suppresses the formation of flat-lying benzene.

Finally, the effect of hydrogen on the catalytic rate of benzene formation on a planar palladium sample collected in a high-pressure reactor incorporated into an ultrahigh-vacuum chamber, is displayed in figure 3. This shows that the benzene formation rate increases with hydrogen pressure corroborating previous results on high-surface-area Pd/Al_2O_3 [12]. Benzene is formed at $P(H_2) = 0$ corresponding to the cyclotrimerization reaction on clean Pd(111). The reaction rate is in good agreement with previous work [4]. The rate of benzene formation increases with increasing hydrogen pressure, where the dependence is linear. It should be emphasized that ethylene is also formed in this reaction [13].

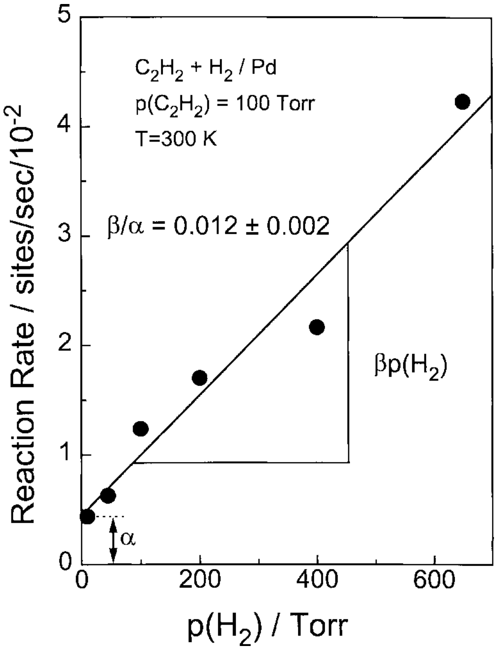

Figure 3. Plot of benzene formation rate as a function of hydrogen pressure catalyzed by Pd(111) using 100 Torr of acetylene as a function of hydrogen pressure.

4. Discussion

The results of figure 1 show that the addition of hydrogen to acetylene causes the ethylidyne coverage on Pd(111) to increase. This is in accord with previous results showing that a vinylidene-covered surface pressurized with hydrogen converts to ethylidyne species [14]. This reaction likely proceeds via a vinyl intermediate which undergoes a hydrogen transfer reaction to form ethylidyne. It may therefore be that, under reaction conditions, ethylidyne is also formed directly from a reaction between adsorbed acetylene and hydrogen to form a vinyl species. Note that the coverage of ethylidyne is measured under steady-state conditions and results from a balance between its formation and removal rates. The ethylidyne coverage appears to saturate at ~0.07 monolayers (~1/3 of the saturation coverage). The origin of this effect is not known. One possible explanation is that the ethylidyne species become more difficult to remove at lower coverages. This effect is evident on Pt(111) where ethylidynes are initially removed rapidly but their rate of removal slows when the surface coverage decreases [18].

The openness of the surface was measured using CO adsorption. This is a common strategy for measuring the number of sites available on supported metal catalysts [19]. These experiments were carried out under a pressure of 5 Torr of CO since a saturation CO coverage is attained at this pressure on vinylidene-covered Pd(111) [10], and at substantially lower pressures on ethylidyne-covered Pd (111) [15]. Thus, all the available palladium surface is likely to be occupied at 5 Torr. The integrated absorbance of the CO feature at ~1850 cm^{-1} [10] increases linearly with hydrogen pressure (figure 1(b)) corresponding to the increased coverage of ethylidyne species on the surface (figure 1(a)). In order to probe the effect of ethylidyne species on benzene formation, acetylene was adsorbed onto ethylidyne-covered/Pd(111) ($\Theta_{\text{ethylidyne}} = 0.25$). The results are summarized in figure 2 and confirm that benzene is formed on the ethylidyne-covered surface. Apparently, the crowded surface causes tilted benzene to be formed. The similarity between the low-temperature 78 amu feature on clean Pd(111) and on ethylidyne/Pd(111) implies that, in this case, benzene is formed via a similar route to that on clean Pd(111), that is, by two acetylenes reacting to form a C_4 intermediate and then reacting with a third to form benzene [3]. In the absence of hydrogen, reaction takes place on a vinylidene-covered surface between adsorbed acetylene and vinylidene [11]. The CO adsorbed on this surface saturates yielding a feature with an integrated absorbance of ~0.01 (figure 1(b)). Ethylidyne species are formed when hydrogen is present resulting in a more open surface allowing more CO to adsorb on the surface. This is illustrated by the linear increase in CO absorbance with increasing hydrogen pressure in figure 1(b)). Assuming that the CO coverage is proportional to the integrated absorbance of the 1850 cm^{-1} feature, the coverage Θ_{tot} is given by

$$\Theta_{\text{tot}} = \Theta_1 + \Theta_2 P(\text{H}_2), \tag{1}$$

where Θ_1 represents the CO coverage on a vinylidene-covered surface, and Θ_2 the coverage on the more open surface containing ethylidyne species per Torr of hydrogen. The data of figure 1(b) show that $\Theta_2/\Theta_1 = 0.007 \pm 0.002\ \text{Torr}^{-1}$. The data of figure 2 demonstrate that benzene is formed rapidly from acetylene on an ethylidyne-covered surface so that the additional space that becomes available when hydrogen is present is available for benzene formation. The slope of the plot of benzene formation rate versus hydrogen pressure (figure 3) is designated β and the intercept, α, so that the rate of benzene formation, R_b, is given by

$$R_\text{b} = \alpha + \beta P(\text{H}_2). \tag{2}$$

The ratio $\beta/\alpha = 0.012 \pm 0.002$. This implies that the increase in the amount of CO due to the addition of hydrogen correlates reasonably well with the observed increase in the rate of benzene formation. These results indicate that the effect of hydrogen on the benzene formation rate is to cause a portion of the vinylidene species to convert into ethylidyne species forming a more open surface. Similar effects are likely also to occur during acetylene hydrogenation to ethylene (which proceeds in parallel with the formation of benzene) where, in this case, hydrogen not only reacts with acetylene to form ethylene but also creates a more open surface.

Finally, note that, although the catalytic reactions were carried out at higher pressures (up to 600 Torr, figure 3) than during the surface analyses (up to 20 Torr, figure 1), the $P(\text{H}_2)/P(\text{C}_2\text{H}_2)$ ratios were in the same range for both experiments.

5. Conclusions

Infrared analyses of a Pd(111) surface during reaction with acetylene and hydrogen show that the ethylidyne coverage increases with increasing hydrogen pressure. This in turn allows more CO to adsorb, where the CO coverage increases linearly with hydrogen pressure. This effect is mirrored in the rate of benzene formation which also increases linearly with hydrogen pressure. Comparing the increase in the amount of CO that can be accommodated onto the surface with the increase in benzene formation rate as a function of hydrogen pressure suggests that the increase in benzene formation activity is due to the more open surface caused by the increase in the amount of ethylidyne present on the surface.

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