On the reaction pathway for the formation of benzene from acetylene catalyzed by palladium

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The reaction between gas-phase acetylene and alumina-supported palladium saturated with ^{13}C-labelled vinylidene is studied using both one-pulse, ^{13}C magic-angle spinning, nuclear magnetic resonance (NMR) spectroscopy and by mass spectroscopic analysis of the reaction products to probe the reaction pathway. The presence of vinylidene on alumina-supported palladium is confirmed by comparing the infrared spectra of the species formed on the supported sample with those found on a Pd(111) single crystal. It is shown using NMR that a high pressure ($\sim$350 Torr) of gas-phase acetylene reacts with adsorbed vinylidene at the same rate at which benzene is formed catalytically on the same sample. The resulting benzene incorporates two ^{13}C atoms. This indicates that benzene is formed by a slow reaction between gas-phase (^{12}C-labelled) acetylene and adsorbed vinylidene ($^{13}CH_2{=}^{13}C{=}$) to form a C_4 intermediate which reacts rapidly with further acetylene to yield benzene. There are precedents for such reactions in homogeneous phase. The proposed reaction pathway differs from that elucidated previously from ultrahigh vacuum studies on clean Pd(111), where it was found that benzene synthesis also proceeds via a C_4 intermediate, in this case formed from two adsorbed acetylenes.

Keywords: nuclear magnetic resonance, vinylidene, palladium, benzene formation, infrared spectroscopy, reaction pathway

1. Introduction

The catalytic synthesis of benzene from acetylene has been widely studied and a rather detailed picture of the reaction pathway has emerged primarily because the reaction is catalyzed by palladium single crystals [1] and benzene is also formed in ultrahigh vacuum from acetylene adsorbed on these samples [2–4]. This, therefore, offers an ideal opportunity to follow the catalytic reaction in detail. Cyclotrimerization is also catalyzed by more conventional, alumina-supported palladium [5] and benzene formation has also been found on other metals [6–8] and titanium oxide [9]. Surface science studies carried out in ultrahigh vacuum have revealed that benzene is formed via a metallocyclic C_4H_4 intermediate [10]. This can further react with a third acetylene to form benzene [11]. The variation in benzene yield as a function of acetylene exposure during temperature-programmed desorption is successfully reproduced by assuming that benzene forms on the (111) face of palladium when adsorbed acetylenes are correctly oriented on the surface [12], and recent scanning-tunnelling microscopy experiments have directly imaged the formation of benzene from acetylene [13]. These results suggest that a rather large ensemble of surface palladium atoms ($\sim$7) is required to form benzene and this is confirmed by studies using gold/palladium alloys [14].

Catalysis using a Pd(111) single-crystal model proceeds with an activation energy of $\sim$2 kcal/mol and via first-order kinetics at a relatively low rate ($\sim 10^{-2}$ reactions/site s) [1]. Acetylene adsorbed on palladium(111) at $\sim$300 K converts into vinylidene ($CH_2{=}C{=}$) [15] implying that benzene is catalytically synthesized on a surface covered with a vinylidene monolayer ($\Theta(\text{saturation}) = 1$ [2]). The presence of this layer completely suppresses further acetylene adsorption in ultrahigh vacuum. It has, however, been shown using sum-frequency generation that ethylene can still adsorb onto an ethylidyne-saturated surface using high external pressures [16–19]. In addition, infrared spectroscopy has been used to demonstrate that carbon monoxide can adsorb onto a Mo(100) surface covered by a thick carbonaceous layer [20,21] and, more recently, onto vinylidene-covered Pd(111) [22]. On the basis of these results, it is proposed that acetylene can also adsorb onto the palladium surface in the presence of a vinylidene overlayer. It is unlikely, however, that the large ensemble required for the reaction on clean palladium is still available on the vinylidene-saturated surface. Recent studies on titanovinylidenes which also coordinate acetylene at the titanium center have demonstrated that acetylene and vinylidene can react to form a C_4H_4 intermediate essentially identical to that found on Pd(111) [23–25]. It is therefore proposed that an analogous pathway operates at high pressure in heterogeneous phase on palladium, where benzene forms by an initial reaction between acetylene adsorbed on a vinylidene-covered surface, and vinylidene itself. This proposal is tested in the following using alumina-supported palladium covered by ^{13}C-labelled vinylidene formed by adsorbing $^{13}C_2H_2$. According to the above hypothesis, this should react with gas-phase acetylene to form benzene causing vinylidene to be removed *at the same rate* at which benzene is formed catalytically with

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the resulting benzene incorporating the ^{13}C labels. Infrared spectroscopy was used to confirm the presence of vinylidene species on the supported sample by comparing the spectrum of acetylene on Pd/Al_2O_3 with the spectrum of a Pd(111) single crystal, both saturated with acetylene at 300 K.

2. Experimental

Pd/Al_2O_3 powder was placed in a small glass vial attached to a cone joint allowing it to be attached to a vacuum system. The sample was cleaned according to literature procedures [26] and, in particular, using the same protocol as used for the infrared experiments described below. The sample is prepared in the NMR vial, saturated with ^{13}C-acetylene at room temperature, evacuated ($<1 \times 10^{-7}$ Torr, 30 min), sealed and stored in liquid nitrogen for subsequent NMR analysis. Note that evacuating the sample for shorter times leaves some residual benzene on the surface as evidenced by the presence of a sharp feature at 128 ppm [27]. Such extensive pumping also ensured that no residual ^{13}C-labelled acetylene remains on the surface and none is detected by NMR or infrared spectroscopy. A similar vinylidene-covered sample was prepared, but in this case was then exposed to ^{12}C-labelled acetylene (345 Torr, 130 s). Nuclear magnetic resonance spectra were collected under magic-angle spinning conditions (MAS) in a 11.7 T static field using a Bruker DRX-500 spectrometer equipped with a Doty 5 mm MAS probe which allowed the sample to be spun at 6 kHz. The conditions for the one-pulse (Bloch decay) experiments were as follows: ^{13}C 90° pulse width 5 μs, relaxation delay 10 s, 2000 transients with high-power proton decoupling (55 kHz). All spectra were externally referenced to the signals of an adamantane powder sample (37.7 and 28.6 ppm from TMS) [28].

Reflection/absorption infrared spectra were collected from a Pd(111) single crystal that had been cleaned using a standard procedure [2] and dosed at 300 K with acetylene. The experimental apparatus and the data collection and analysis protocols have been described in detail elsewhere [29]. The infrared spectra of acetylene and ethylene on supported palladium (5% Pd/Al_2O_3, Alfa Products) were collected using a Perkin–Elmer spectrometer operating in transmission mode. The Pd/Al_2O_3 powder was pressed into a pellet and mounted onto a transfer rod which was enclosed in an evacuated cell described elsewhere [30]. The sample was cleaned by heating in oxygen (150 Torr, 525 K) and then reduced twice in hydrogen (150 Torr, 575 K) following which the cell was evacuated overnight. An identical procedure was used for the NMR samples (see above) [26]. A background sample was collected and the sample then saturated with ethylene (10 Torr, 150 s) or acetylene (10 Torr, 150 s) and the spectrum recorded using exactly identical geometries.

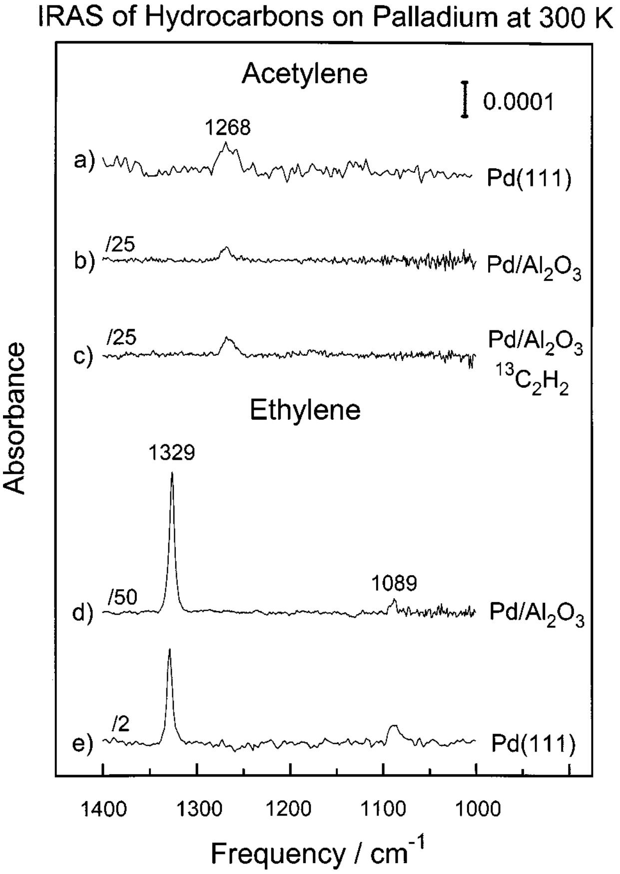


Figure 1. Infrared spectra of (a) acetylene adsorbed on a Pd(111) single crystal, (b) $^{12}C_2H_2$ adsorbed on 5% Pd/Al_2O_3, (c) $^{13}C_2H_2$ adsorbed on 5% Pd/Al_2O_3, (d) ethylene adsorbed on 5% Pd/Al_2O_3 and (e) ethylene adsorbed on Pd(111).

3. Results and discussion

The formation of vinylidene on supported palladium is confirmed by the data of figure 1. Figure 1(a) displays a reflection–absorption infrared (RAIRS) spectrum of a Pd(111) sample saturated with acetylene at 300 K. This exhibits a single feature at 1268 cm^{-1} which is assigned to the CH_2 bending mode of vinylidene [31]. The corresponding spectrum for alumina-supported palladium saturated with acetylene (10 Torr, 150 s) is displayed in figure 1(b) along with the spectrum found by adsorbing ^{13}C-labelled acetylene onto Pd/Al_2O_3 (figure 1(c)). The spectra on Pd(111) and supported palladium are identical confirming the formation of vinylidene on alumina-supported palladium. The lack of a significant frequency shift of the feature from ^{13}C-labelled acetylene confirms its assignment to a CH_2 mode. In fact, there is no measurable frequency shift for this peak. This would be expected following labeling of the carbon but is not detectable because of its low intensity and relatively large width which means that infrared spectroscopy is not useful for following the replacement of labelled vinylidene on the surface. For comparison, figure 1(d) displays the infrared spectrum collected fol-

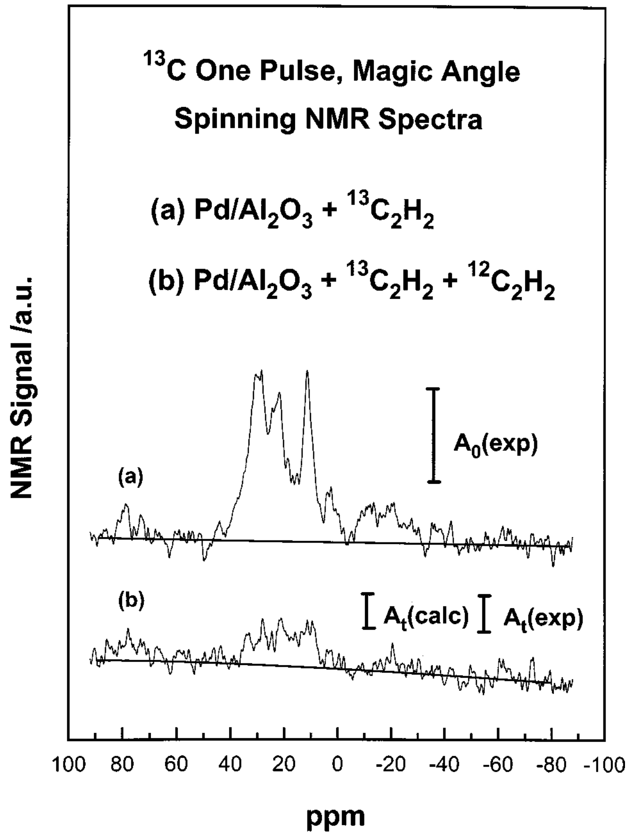


Figure 2. ^{13}C one-pulse, magic-angle spinning NMR spectra collected (a) following the adsorption of $^{13}C_2H_2$ at 300 K on 5% palladium supported on alumina and (b) after that sample had reacted with normal acetylene (300 K, 3445 Torr, 130 s).

lowing exposure of alumina-supported palladium to ethylene (10 Torr for 150 s) which displays the characteristic methyl bending mode at 1329 cm^{-1} and the C–C stretching mode at 1089 cm^{-1}. These features are also detected on a palladium single crystal saturated with ethylene (figure 1(e)) [29]. These results confirm that acetylene adsorption on palladium does not lead to the formation of ethylidyne, and similar ethylidyne formation has been found previously on alumina-supported palladium following ethylene adsorption [32].

Nuclear-magnetic resonance is used to follow changes in vinylidene coverage on supported palladium since it is sensitive only to ^{13}C nuclei. The ^{13}C MAS NMR, one-pulse spectrum of ^{13}C-acetylene-saturated, alumina-supported palladium is displayed in figure 2(a). Clear adsorbate features are evident between 10 and 40 ppm assigned to the presence of vinylidene on the surface. Note that this chemical shift corresponds to sp^3-hybridized carbons [28]. However, since the vinylidene is tilted with respect to the surface [15], this may result in substantial vinylidene rehybridization due to π-orbital overlap with the surface. The vertical bar adjacent to figure 2(a) represents the area under the NMR feature due to vinylidene prior to reaction with ^{12}C-labelled acetylene (designated A_0(exp)) and is taken to be proportional to the initial ^{13}C-labelled vinylidene coverage.

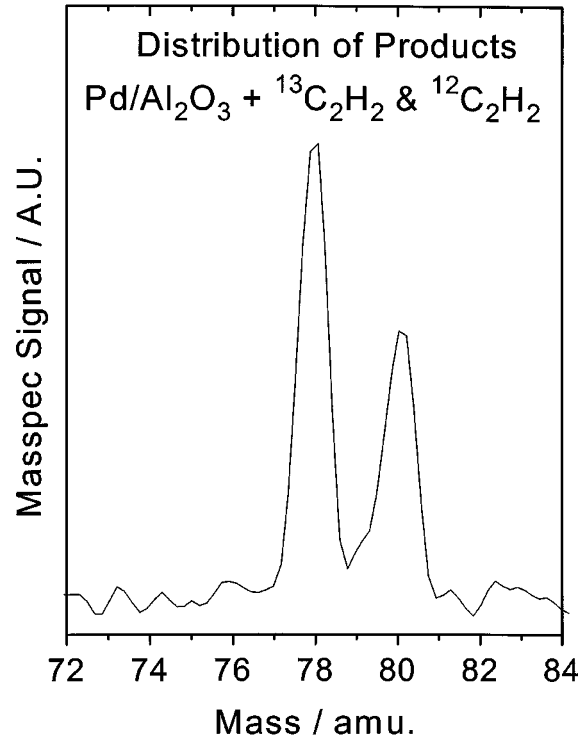
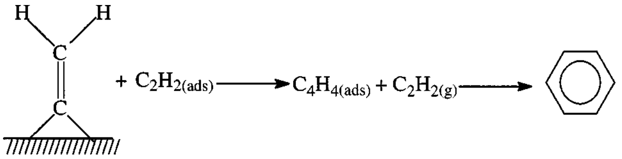


Figure 3. Mass spectrum of the benzene formed in the reaction between normal acetylene (300 K, 345 Torr, 130 s) and a ^{13}C-labeled, vinylidene-covered sample showing the region between 72 and 84 amu.

Figure 2(b) displays the corresponding spectrum of a vinylidene-covered Pd/Al_2O_3 sample that has been exposed to $^{12}C_2H_2$ (345 Torr, 130 s). Based on the above proposal, this should react with ^{13}C-labelled vinylidene, titrating it from the surface at exactly the same rate at which benzene is synthesized by the same catalyst. The above $^{12}C_2H_2$ exposure, therefore, on the basis of catalytic turnover frequencies measured for Pd(111) [1], corresponds to the dose required to remove ~70% of the original ^{13}C-labelled vinylidene. The amount calculated on this basis to remain following reaction with ^{12}C-labelled acetylene is indicated by a vertical bar (labelled A_t(calc)) and that measured experimentally following exposure to $^{12}C_2H_2$ is designated by a bar labelled A_t(exp) (and, as noted above, corresponds to the removal of ~70% of the initially adsorbed, labelled vinylidene). The agreement between these latter values is very good, which demonstrates that the rate of vinylidene removal by reaction with gas-phase acetylene equals the rate at which benzene is formed catalytically.

Figure 3 displays the mass spectrum of the benzene formed by the reaction between $^{12}C_2H_2$ and a ^{13}C-vinylidene-covered, Pd/Al_2O_3 surface. There is significant intensity at 78 amu corresponding to the formation of $^{12}C_6H_6$. This arises from reaction of gas-phase acetylene with ^{12}C-labelled vinylidene species that have replaced the ^{13}C-labelled ones. However, there is also a large signal present at 80 amu corresponding to the formation of $^{13}C_2{}^{12}C_4H_6$, so that the labelled vinylidene removed by reaction with acetylene is indeed incorporated into the benzene that is formed. The proposed reaction pathway for the palladium-catalyzed formation of acetylene is summarized as follows:



This pathway is consistent with the observations that (i) acetylene reacts with labelled vinylidene at the same rate at which benzene is formed and (ii) two ^{13}C atoms are incorporated into the resultant benzene. It also provides an explanation of why the vinylidene-covered surface is active for acetylene cyclotrimerization, while the results on the clean surface appear to suggest that the reaction requires a relatively large number of exposed palladium atoms to assemble a benzene molecule from acetylene.

4. Conclusions

It is shown that the reaction pathway for the formation of benzene under high-pressure, catalytic conditions differs from that established in ultrahigh vacuum since the catalytically active surface is covered by vinylidene species. This dense layer (Θ(saturation) $= 1.0$ [2]) still allows acetylene to adsorb on the palladium surface at sufficiently high pressures. Furthermore, nuclear magnetic resonance studies of a labelled, vinylidene-covered surface reveal that vinylidene is removed from the surface at the same rate at which benzene is formed catalytically. This indicates that the reaction pathway under catalytic conditions involves an initial reaction between acetylene and vinylidene eventually forming benzene. Mass spectral analysis of the benzene that is formed by the reaction of gas-phase, ^{12}C-labelled acetylene with a ^{13}C-labelled vinylidene overlayer is in accord with this reaction scheme. The results also indicate that the rate-limiting step in the catalytic synthesis of benzene from acetylene is the adsorption and reaction of gas-phase acetylene with adsorbed vinylidene.

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