Catalysis Today 65 (2001) 3–11

www.elsevier.com/locate/cattod

Palladium-catalyzed cyclotrimerization and hydrogenation: from ultrahigh vacuum to high-pressure catalysis

Dario Stacchiola, Hebert Molero, W.T. Tysoe*

Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, P.O. Box 413, Milwaukee, WI 53201, USA

Abstract

The surface reactions involved in the palladium-catalyzed formation of benzene from acetylene are discussed as an example of the way in which such strategies can be used to understand catalytic reaction pathways in detail. This provides an ideal system for surface science/catalysis studies since benzene is formed both in ultrahigh vacuum in temperature-programmed desorption and under high-pressure, catalytic conditions. It is found that benzene is synthesized on clean Pd(1 1 1) by an initial fast reaction between two adsorbed acetylene molecules to yield a tilted C_4H_4 metallacyclic intermediate. This reacts with a third acetylene to form benzene and the hexagonal (1 1 1) surface of palladium acts as a template for the reaction. Under catalytic conditions, however, it is found that a relatively unreactive vinylidene layer covers the surface. Organometallic studies show that acetylene and vinylidene can react to form a C_4H_4 intermediate analogous to that found to form from acetylene on a palladium surface. This suggests an alternative possible reaction pathway under catalytic conditions in which acetylene and vinylidene react to eventually form benzene. This proposal is confirmed using nuclear magnetic resonance analysis of a ^{13}C-labelled vinylidene-covered surface. It is also shown that the vinylidene species formed from acetylene and ethylidyne species formed from ethylene can react with hydrogen at high pressures where the ethylidyne removal rate is found to be first-order in hydrogen pressure. This behavior is used to explain the hydrogen pressure dependence during catalysis where the hydrogen performs two roles, that of reactant, and to remove carbonaceous species from the surface. Finally, it is found that vinylidene also reacts with hydrogen at high pressures where it is removed *via* the formation of ethylidyne. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ultrahigh vacuum; Palladium-catalyzed; Cyclotrimerization; Hydrogenation

1. Introduction

Palladium-catalyzed acetylene cyclotrimerization and alkene and alkyne hydrogenation provide ideal candidates for fundamental investigations of catalytic reaction pathways. This is because these reactions proceed in ultrahigh vacuum where, for example, benzene is formed in temperature-programmed desorption when a Pd(1 1 1) single crystal is saturated with acetylene [1], and adsorbed atomic hydrogen reacts with acetylene to yield ethylene [2]. In addition, a palladium single crystal catalyzes these reactions at high pressures with identical kinetics as supported systems. Acetylene cyclotrimerization was first referred to (to our knowledge) in 1915 [3]. Subsequent studies introduced the proposition that one of the roles of the catalyst was to provide a structural template for benzene synthesis [4] as well as lowering the reaction activation energy. This notion was later borne out experimentally where various tailored surface structures could be fabricated by carefully cutting single crystals to form faces with known orientations [5].

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* Corresponding author. Tel.: +1-414-229-5222;
fax: +1-414-229-5036.
E-mail address: wtt@uwm.edu (W.T. Tysoe).

PII: S0920-5861(00)00539-3

These experiments clearly demonstrated that the hexagonal (1 1 1) face of palladium was far more active for the synthesis of benzene from acetylene than others [6,7] where the yield of benzene on Pd(1 1 1) is ∼10 times larger than that on Pd(1 0 0) [9] and essentially no benzene is produced on Pd(1 1 0) [7].

In the early 1980s, it was shown that a monolayer of acetylene chemisorbed on Pd(1 1 1) reacted to form benzene, a result published almost simultaneously by three groups [1,8–10]. Although the reaction, in this case, is not catalytic, this discovery provided an ideal test system for studying a reasonably complicated organic synthetic reaction pathway in some detail, using a wide array of surface sensitive strategies. Subsequently, several surfaces were found to catalyze the same reaction [11–14].

Palladium-catalyzed hydrogenation of ethylene and acetylene are classical catalytic reactions that have been studied for many years where it has been established that adsorbed atomic hydrogen adds across the double or triple bond of the adsorbed hydrocarbon [15–26]. This proposal has been confirmed by subsequent surface science studies [2].

The following paper outlines how surface science strategies have resulted in the discovery of various surface species on the (1 1 1) face of palladium and how their roles in the catalytic reaction have been identified. This surface analytical information has been used to paint a picture of the working, catalytically active surface, postulate plausible catalytic reaction pathways, and test them.

In particular, these results have revealed that the active catalyst is no longer a clean single crystal but is covered by a strongly bound, saturated overlayer of a carbonaceous species, the nature of which depends on the particular metal and reactants. The role of these species in the catalytic reaction is also discussed.

2. Experimental

A wide range of ultrahigh vacuum experimental strategies was used to attack the problem of understanding the catalytic pathway for the synthesis of benzene from acetylene. These have all been discussed in detail elsewhere. These include high-pressure catalytic reactions to monitor reaction kinetics at high-pressure [27] and temperature-programmed desorption (TPD) to monitor similar effects in ultrahigh vacuum [1,10]. Surface species have been scrutinized by X-ray and ultraviolet photoelectron spectroscopies [1] and using reflection-absorption infrared spectroscopy (RAIRS) on single crystal samples [28] and infrared spectroscopy on high-surface-area samples [29,30].

More recently, laser-induced thermal desorption (LITD) [31–33] and nuclear magnetic resonance spectroscopies [34] have been used to monitor the nature of the surface species. These results have combined to provide a picture of the nature of the catalytically active surface and the reaction pathway.

3. Results

3.1. Model acetylene cyclotrimerization catalysts

The conversion of acetylene to benzene is catalyzed by alumina-supported palladium at 540 K [35] where the catalytic reaction declines from an extremely high initial rate on the freshly prepared catalyst, where acetylene conversions approach 100%, decreasing to a steady-state rate conversion of ∼3% after long reaction times. The reaction, therefore, appears to self-poison. A portion of the initial high benzene formation activity can be restored by the addition of hydrogen [35]. The reaction kinetics have also been measured using a low-surface-area Pd(1 1 1) single crystal which catalyzes the reaction at a turnover frequency of $\sim 10^{-2}$ reactions/site/s, where a site is defined as an exposed palladium atom on the (1 1 1) face [27]. Since any transient due to “poisoning” of the surface will very quickly completely stabilize on such a small-area sample, this is taken to correspond to the low steady-state rate found at long times on the high-surface-area catalyst. The reaction kinetics were also measured in detail where the rate was found to be first-order in acetylene pressure and to have a temperature dependence yielding a relatively low activation energy of ∼2 kcal/mol [27]. An important goal is, therefore, to rationalize this behavior in the context of the chemistry found in ultrahigh vacuum.

3.2. The reaction pathway to benzene formation on Pd(1 1 1)

Fig. 1 displays a series of benzene (78 amu) temperature-programmed desorption (TPD) spectra

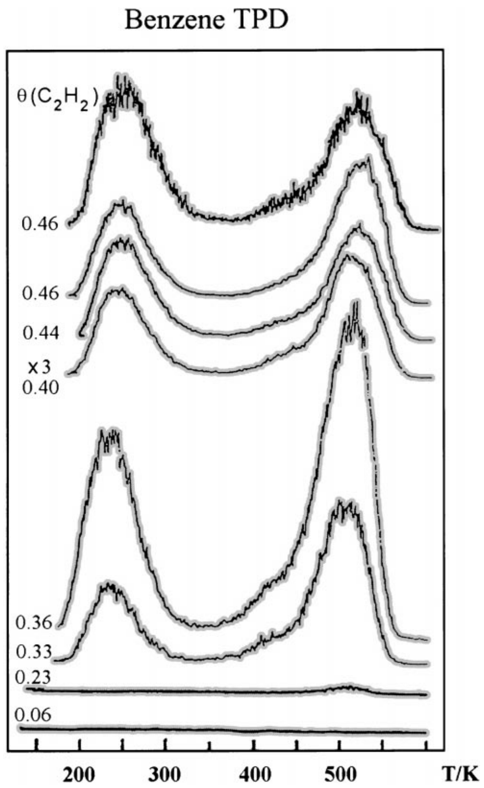


Fig. 1. Benzene (78 amu) temperature-programmed desorption spectra collected following exposure of a Pd(1 1 1) surface to acetylene at 100 K. The spectra were collected at a heating rate of 10 K/s and the acetylene coverages are marked adjacent to each spectrum, where the acetylene coverage is referenced to the number of exposed palladium atoms on the (1 1 1) face.

collected following exposure of a clean Pd(1 1 1) surface to acetylene [1,10]. The resulting acetylene coverages are marked adjacent to each spectrum, where these are normalized to the atom site density on the (1 1 1) face. Here the saturation acetylene coverage is 0.46 monolayers [1]. Benzene desorbs in two peaks with a low-temperature state at ∼260 K and a high-temperature state at ∼520 K. Both of these can be reproduced by adsorbing benzene on the Pd(1 1 1) surface [36] so that the rate-limiting step in the formation of benzene in TPD is product desorption. This implies that benzene was synthesized at lower temperatures (below ∼200 K). Direct spectroscopic evidence also points to low-temperature formation of benzene from acetylene [8]. The maximum benzene yield in temperature-programmed desorption when the surface is saturated with acetylene, corresponds to the conversion of ∼30% of the adsorbed acetylene with a sample heating rate of ∼10 K/s. When the heating rate is substantially lowered and the acetylene conversion monitored using laser-induced thermal desorption (LITD), conversions can approach 100% [31–33]. This suggests a branching reaction for the adsorbed acetylene where the branching ratio is modified by changing the heating rate.

Adsorbed acetylene distorts on Pd(1 1 1) below 200 K so that the carbon atoms are sp^2 hybridized [37–39]. It has further been demonstrated, by adsorbing dichlorocyclobutene, that benzene forms by reaction between acetylene and an intermediate having a stoichiometry C_4H_4 [40,41]. Near-edge X-ray adsorption fine structure (NEXAFS) results, in conjunction with theoretical analyses of these data, allows this species to be identified as a metallacycle [42]. The “template” effect of the hexagonal (1 1 1) face correctly orients the adsorbed C_2H_2 and C_4H_4 species to form benzene [4]. These ideas suggest that the synthesis of benzene in ultrahigh vacuum requires the participation of ∼7 exposed palladium atoms on the surface. A similar model successfully rationalizes the effect of site blocking by oxygen [43] and the formation of Au/Pd alloy surfaces [44,45] on the benzene yield. Further confirmation of the participation of C_4 species in the reaction comes from the desorption of heterocyclic products, furan and thiophene, when acetylene is co-adsorbed with oxygen and sulfur, respectively [43,46].

3.3. Model acetylene hydrogenation catalysts

A palladium single crystal catalyzes acetylene hydrogenation at high pressures with kinetics that strongly resemble those measured on alumina-supported palladium. The activation energy for the reaction (∼9 kcal/mol, [47]) is typical for noble-metal-catalyzed hydrogenation reactions [15–26]. The reaction order in hydrogen pressure is ∼1.04 at 300 K, a value again in good agreement with that found for supported catalysts. This reaction order increases with reaction temperature so that at 360 K the order is 1.25 in hydrogen pressure. This effect has also been noted for supported catalysts. A negative reaction order is found in acetylene pressure, which is again typical for alkene and alkyne hydrogenation reactions [15–26].

3.4. *Acetylene hydrogenation in ultrahigh vacuum*

Acetylene adsorbed onto a hydrogen-covered Pd(1 1 1) surface reacts to form ethylene with an activation energy of 5.4 kcal/mol, a value lower than that found catalytically at high pressures (see Section 3.3). The reaction is found to be first-order in hydrogen coverage in accord with the proposal by Horiuti and Polanyi [48].

3.5. *The nature of the catalytically active surface*

The adsorbed acetylene and C_4H_4 species discussed in the previous section are present on the surface at $\leq$200 K. On heating, these convert to another species, identified as a vinylidene adsorbed with its axis tilted with respect to the surface [1,49]. Measurement of its adsorption kinetics on Pd(1 1 1) at 300 K, where this species forms almost exclusively, reveals that it adsorbs *via* precursor-state kinetics with an initial sticking probability of $\sim$1 leading to a saturation coverage $\theta_{\mathrm{max}} = 1.0$ [1], where again coverages are referenced to the palladium atom density of the (1 1 1) face. The species is unreactive in ultrahigh vacuum so that heating a vinylidene-covered surface merely desorbs hydrogen at $\sim$450 K and no benzene is formed [1]. In addition, co-adsorption of acetylene and hydrogen on Pd(1 1 1) at $\sim$100 K desorbs ethylene so that the flat-lying, rehybridized acetylenic species is the precursor to acetylene hydrogenation, whereas co-adsorbing hydrogen and vinylidene yields no hydrogenation products in temperature-programmed desorption [2]. This suggests that the accumulation of unreactive vinylidene species might be responsible for the decrease in cyclotrimerization activity as a function of time found for supported palladium catalysts referred to above [35]. Adsorption of ethylene on Pd(1 1 1) leads to the formation of a similarly unreactive ethylidyne (CH_3–C≡) species which adsorbs with a saturation coverage of 0.25 [50,51].

3.6. *Properties of the catalytically active surface: trimerization pathway and kinetics*

These results indicate that benzene is rapidly synthesized from acetylene on clean Pd(1 1 1) *via* a reaction between a C_4 and C_2 species and that an ensemble of $\sim$7 palladium atoms is required for this reaction. During catalysis, however, reaction apparently proceeds in the presence of a carbonaceous layer which, when the reaction is carried out at low enough temperatures, consists of vinylidene. The following section addresses the properties of this layer and proposes a reaction pathway for benzene formation based on the reaction route on Pd(1 1 1) in ultrahigh vacuum, but modified to take into account the presence of the vinylidene layer.

As noted above, vinylidene saturates the surface at a coverage, θ_{sat} (vinylidene) $= 1.0$ [1], so that no further molecules adsorb when the surface is exposed in ultrahigh vacuum. It has, however, been demonstrated that ethylene adsorbs on an ethylidyne-covered Pt(1 1 1) surface when the ethylene pressure is sufficiently high [52–55] and that CO can adsorb onto Mo(1 0 0) covered by a thick carbonaceous layer [56].

In order to explore whether a vinylidene layer can accommodate additional molecules under higher-pressure conditions, CO adsorption was also used as a probe. CO does not adsorb onto a vinylidene-covered surface when exposed in ultrahigh vacuum (at pressures of $\sim 10^{-7}$–10^{-8} Torr). However, when the surface is pressurized with several Torr of CO, CO vibrations are detected at $\sim$1800 cm^{-1}. The variation in signal intensity is plotted as a function of CO pressure in Fig. 2. Now CO adsorbs reversibly on vinylidene-covered Pd(1 1 1) and saturates at pressures of $\sim$3 Torr. The presence of vinylidene has modified, but not completely suppressed, CO adsorption on Pd(1 1 1). CO saturates a *clean* Pd(1 1 1) surface after an exposure of $\sim$2 L [57,58] and desorbs at $\sim$520 K. When the surface is covered by vinylidene, CO adsorbs reversibly at 300 K and saturates only when an external pressures of $\sim$4 Torr is applied. Note that this behavior is now closer to that encountered on supported catalytic systems. These results indicate that the saturated vinylidene layer is sufficiently flexible to accommodate a significant amount of additional CO. These results also imply that acetylene should also adsorb onto a vinylidene-covered surface, although it is unlikely that two or three adjacent acetylene molecules can be accommodated as suggested, from ultrahigh vacuum data, is necessary for benzene synthesis. However, it has been shown that acetylene and vinylidene can react, in homogenous phase, to form a C_4 intermediate in titanium-containing molecules [59–61]. It is, thus, suggested that acetylene adsorbed

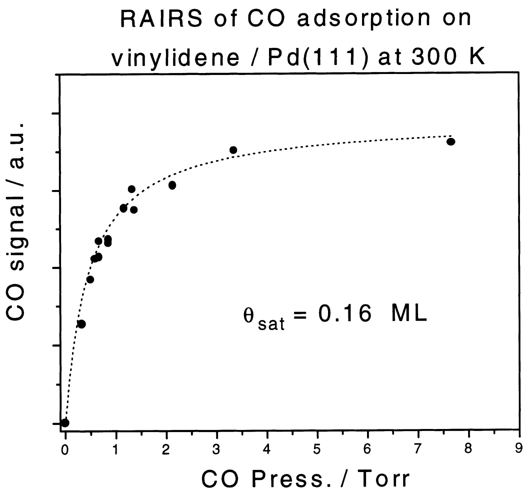
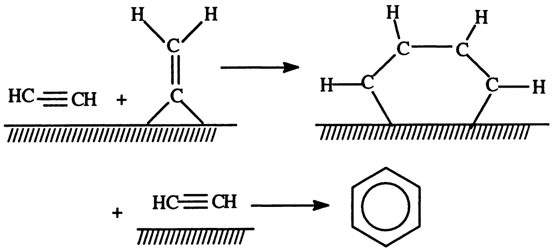


Fig. 2. Adsorption isotherm for CO on a vinylidene-saturated Pd(1 1 1) surface collected at a sample temperature of 300 K. The saturation coverage calculated from the integrated absorbance of CO compared to that on the clean surface is estimated to be ~0.16 monolayers.

on the vinylidene-covered palladium surface can analogously react to form a C_4 species as follows:



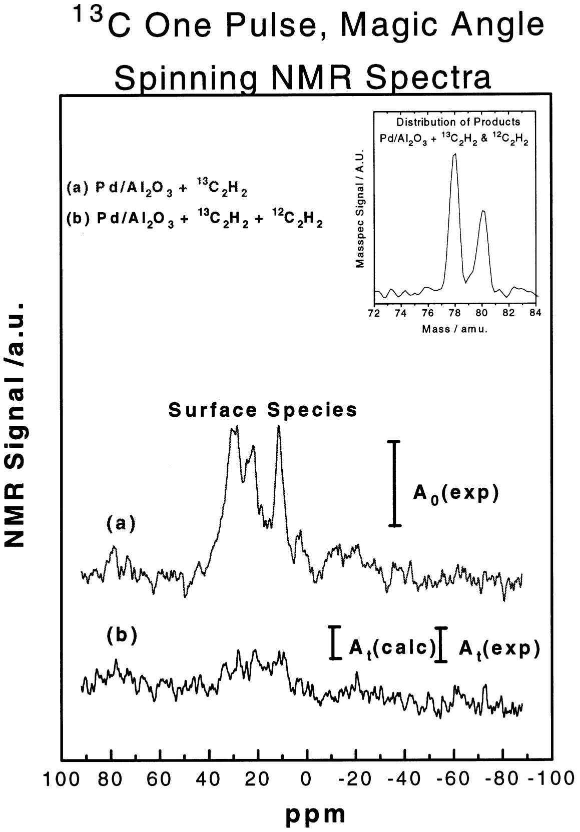


Fig. 3. ^{13}C-magic-angle-spinning NMR spectra of vinylidene formed on alumina-supported palladium (a), and after exposure to $^{12}C_2H_2$ (345 Torr, 130 s) (b). Shown as an inset is a mass spectrum of the benzene that is formed.

This is then proposed to react rapidly with a third acetylene to form benzene. In order to test this hypothesis, a vinylidene-covered surface is prepared using ^{13}C-labelled acetylene. Nuclear magnetic resonance was used to monitor the presence of ^{13}C-labelled vinylidene and, in order to provide sufficient nuclei to collect the spectra, these were grown on high-surface-area palladium supported on alumina. Infrared spectra were collected following exposure to $^{12}C_2H_2$, which gave the characteristic vibrational spectrum due to the formation of vinylidene [34]. The corresponding ^{13}C magic-angle-spinning (MAS) NMR spectrum is displayed in Fig. 3(a). A sharp feature is also detected at 128 ppm due to benzene [62]. The spectrum of the adsorbed layer clearly reveals features due to the presence of ^{13}C-containing surface species, the chemical shift corresponding to ~sp^3 hybridized carbon [63]. Note that the π-overlap of the carbon–carbon double bond with the surface could well result in significant rehybridization so that this feature is assigned to the presence of vinylidenes. According to the above postulate, these should react with $^{12}C_2H_2$ to yield benzene. Moreover, they should be titrated from the surface at the same rate at which benzene is catalytically synthesized. The vinylidene-covered sample was, therefore, exposed to $^{12}C_2H_2$ (345 Torr, 130 s). This exposure was calculated on the basis of the experimental benzene formation rate, as the time required to remove ~70% of the adsorbed vinylidenes [27]. The ^{13}C NMR signal collected following this procedure is displayed in Fig. 3(b). The *initial* integrated intensity of the NMR feature is represented by a vertical bar indicated in Fig. 3 as A_0(exp). The *calculated* remaining area, following $^{12}C_2H_2$ exposure as described above, is represented by a vertical bar indicated as A_t(calc) and the corresponding experimental value is represented as A_t(exp) and is measured from the integrated area under the curve displayed in Fig. 3(b). The agreement between the experimental and calculated values is extremely good, confirming that ^{13}C-labelled vinylidene reacts with $^{12}C_2H_2$ at exactly the same rate at which benzene is formed. Shown as an inset in Fig. 3 is a mass spectrum of the benzene that is formed. In addition to the 78 amu peak for $^{12}C_6H_6$, this shows a feature at 80 amu corresponding to the presence of $^{12}C_4{}^{13}C_2H_6$ where the ^{13}C arises from vinylidene pre-adsorbed on the surface. This confirms that adsorbed acetylene and a vinylidene can react to yield a C_4-intermediate that finally reacts with gas-phase acetylene yielding benzene.

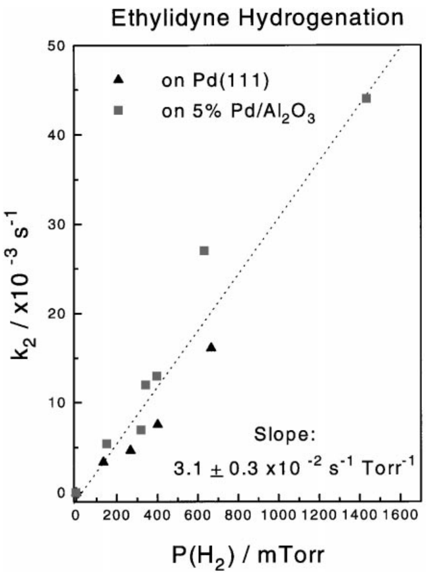


Fig. 4. Plot of the ethylidyne hydrogenation rate constant on Pd(1 1 1)and Pd/Al_2O_3 as a function of hydrogen pressure.

3.7. Effect of hydrogen on the carbonaceous layer

It has been shown previously that the ethylidyne species present on the surface during ethylene hydrogenation, although unreactive in ultrahigh vacuum, can react with high pressures of hydrogen [29,30]. This is illustrated in Fig. 4, which plots the rate of ethylidyne hydrogenation as a function of hydrogen pressure where the ethylidyne coverage is monitored using infrared spectroscopy. These experiments were performed for both Pd(1 1 1) and Pd/Al_2O_3 where the reaction rates are identical for both samples. Furthermore, the ethylidyne-removal rate constant varies linearly with hydrogen pressure suggesting a first-order reaction. This result indicates that the ethylidyne coverage should vary with hydrogen pressure, the coverage decreasing with increasing pressure. Since the presence of the carbonaceous layer suppresses ethylene adsorption onto the surface, this in turn implies that the ethylene coverage should increase with hydrogen pressure. The result of this effect on the kinetics of palladium-catalyzed ethylene hydrogenation is illustrated in Fig. 5. Assuming that ethylene hydrogenates by a stepwise addition of hydrogen [48], and that hydrogen adsorbs dissociatively on Pd(1 1 1), predicts that the reaction rate should be proportional to $\sqrt{P(H_2)}$. A plot of Rate/$\sqrt{P(H_2)}$ versus $P(H_2)$ should, therefore, lead to a horizontal line. In contrast, the data in Fig. 5 show that this increases with hydrogen pressure and this effect is in accord with the proposal

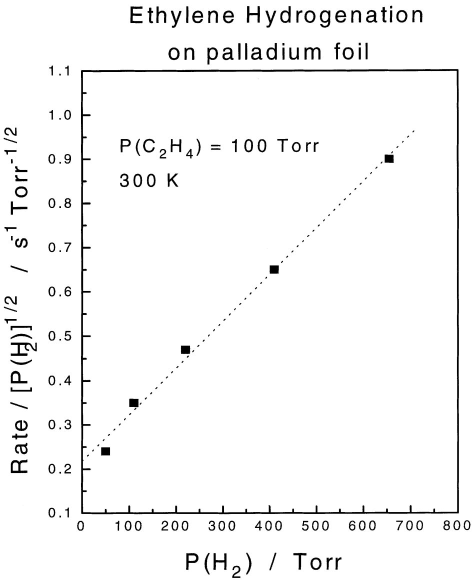


Fig. 5. Plot of Rate/$\sqrt{P(H_2)}$ vs. $P(H_2)$ for palladium-catalyzed ethylene hydrogenation.

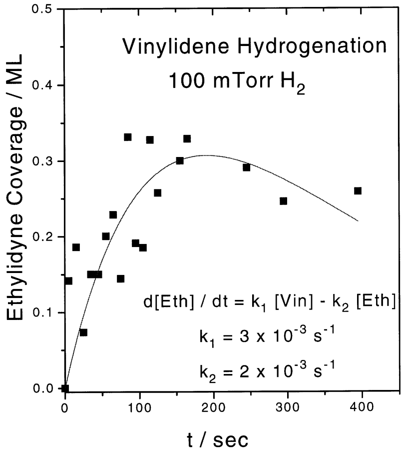
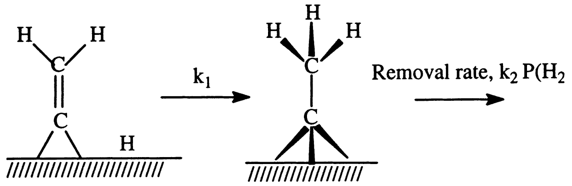


Fig. 6. Plot of ethylidyne coverage vs. time from reaction of a vinylidene-covered Pd(1 1 1) surface with hydrogen.

that additional ethylene can be accommodated onto the surface because ethylidynes have been removed.

Monitoring a Pd(1 1 1) single crystal during acetylene hydrogenation reveals not only vinylidene species but also ethylidynes. This effect can be probed by reacting a vinylidene-covered Pd(1 1 1) surface with hydrogen. It is found that ethylidyne species are formed and the time variation of the ethylidyne coverage is plotted in Fig. 6. This shows that the ethylidyne coverage from a reaction of a vinylidene-covered Pd(1 1 1) surface with 0.1 Torr of hydrogen initially increases and subsequently decreases suggesting a sequential reaction:



The value of k_2 is known from the data of Fig. 4 so that these data can be fit to a single rate constant k_1. These values are shown plotted in Fig. 7 versus hydrogen pressure and again show a linear variation. Interestingly, the reaction rate constant k_1 is $3.2 \pm 0.5 \times 10^{-2}$/s/Torr, identical to that for ethylidyne removal (k_2). This is interpreted by realizing that the saturation coverage of vinylidene is 1.0 (where coverages are referenced to the palladium atom density on the (1 1 1) face) compared with 0.25 monolayers for the saturation coverage of ethylidyne. This suggest that the conversion of vinylidene to ethylidyne is limited by the space available on the palladium surface.

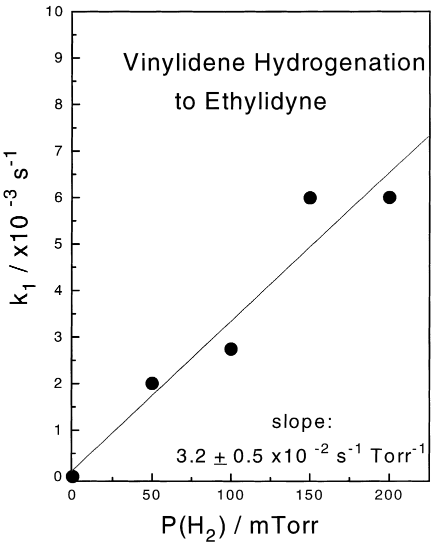


Fig. 7. Plot of k_1 vs. hydrogen pressure.

4. Conclusions

A model for the palladium-catalyzed cyclotrimerization is proposed, based on a combination of knowledge of the reaction pathway found under ultrahigh vacuum conditions and of the nature of the surface present under catalytic conditions. It is proposed that acetylene can still adsorb onto the Pd(1 1 1) surface in spite of the presence of a vinylidene layer and that the adsorbed acetylene can react with vinylidene to yield a C_4H_4 intermediate analogous to that found in ultrahigh vacuum. These strongly bound species also react with hydrogen which may therefore play a dual role in hydrogenation catalysts, first as a reactant but also to remove the carbonaceous layer from the surface allowing further access of the reactants.

Acknowledgements

We gratefully acknowledge support of this work by the US Department of Energy, Division of Chemical

Sciences, Office of Basic Energy Sciences, under grant number DE-FG02-92ER14289. We also acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. DS gratefully acknowledges a fellowship from the Argentine Culture and Education Ministry, DNCI.

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