Simulation of benzene formation from acetylene on palladium and oxygen-covered palladium surfaces

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Abstract

Acetylene cyclotrimerization catalyzed by palladium has been shown to proceed via the initial rapid formation of a C_4H_4 species. This can either react with adsorbed acetylene to form benzene or alternatively, as has been recently suggested, it can dimerize forming cyclooctatetraene which decomposes to yield benzene. Trimerization is sufficiently fast that reaction is desorption rather than surface reaction rate limited so that the nature of the ensembles to benzene formation can be simulated assuming that acetylene molecules adsorb randomly on the surface. Calculating the number of properly oriented triads on Pd(111) correctly predicts the benzene yield observed in temperature-programmed desorption as a function of initial acetylene coverage for both Pd(111) and oxygen-covered Pd(111) and suggests that cyclooctatetraene formation, at best, provides only a minor route to the synthesis of benzene. The nature of the acetylene environment around each reactively formed benzene can also be interrogated and these results suggest that the majority ($\sim 90\%$) of the reactively formed benzene is sterically crowded on the surface but that this crowding is relieved by the conversion of acetylene to vinylidene species between ~ 200 and 300 K. Finally, the structure sensitivity of benzene formation found in temperature-programmed desorption experiments is addressed.

1. Introduction

Palladium-catalyzed formation of benzene from acetylene is a particularly interesting reaction since it takes place both in ultra-high vacuum, where a significant amount of benzene is detected in thermal desorption following acetylene adsorption on Pd(111) [1–3], and at higher pressures where benzene can be synthesized from acetylene using either a model single crystal [4,5] or dispersed metal catalysts [6]. Since the reaction proceeds in ultra-high vacuum, the reaction pathway can be probed in some detail [1–10]. It has been shown that the first step is the rapid formation of a stable C_4H_4 intermediate which has been identified spectroscopically on the surface and its existence confirmed theoretically [7–9]. This has been proposed to react with adsorbed acetylene [10] to form benzene [11,12], although more recently it has been suggested that two C_4 species can combine to form cyclooctatetraene that thermally decomposes to yield benzene and acetylene [8,13,14]. There are

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several intriguing aspects about the reaction that will be addressed in the following. First, the apparently facile formation of thermodynamically stable C_4 species results in only approximately 30% of the adsorbed acetylene forming benzene [1,10] with the remainder reacting to form adsorbed vinylidene [15] that thermally decomposes at ~ 450 K to evolve hydrogen and to deposit carbon onto the surface [1]. Second, it is found that benzene desorbs in two very distinct states, one at ~ 280 K the other at a considerably higher temperature (520 K) [1,2,12]. The low-temperature state has been attributed to the desorption of sterically crowded benzene which has been suggested to adopt a tilted configuration [16]. This state has been reproduced on Pd(111) by using large benzene exposures [17,18]. The high-temperature (520 K) state is due to the desorption of benzene oriented parallel to the (111) surface of palladium and this state can also be reproduced by adsorbing benzene directly onto the palladium surface. These results indicate that both of the benzene thermal desorption states found by dosing Pd(111) with acetylene are desorption-rate limited. This result has been confirmed by co-adsorbing isotopically labeled benzene (C_6D_6) with C_2H_2 since both C_6D_6 and C_6H_6 desorb with identical profiles [11].

Ormerod and Lambert [19] have also shown that pre-covering Pd(111) with oxygen reduces the total benzene yield very considerably. These results have been interpreted by assuming that the oxygen merely blocks sites and only minimally affects the reactivity of the acetylene. The simulations performed in the following confirm this result and correctly predict the decrease in benzene yield as a function of oxygen coverage.

The reaction also shows a strong structure sensitivity, both in ultra-high vacuum and at high pressures. This was first demonstrated by Gentle and Muetterties who showed that Pd(111) was the most active surface for the formation of benzene, Pd(100) the least active with Pd(110) intermediate between the two [2,4,20]. Interestingly the reactivity in ultra-high vacuum did not correlate well with the corresponding structure sensitivity of the catalytic reaction. In more recent work, Yoshinobu et al. [21] have suggested that Pd(110) is essentially unreactive for benzene formation in ultra-high vacuum, a result that correlates more closely with that found at high pres-

sures. It was suggested that the apparent rather high benzene yield for Pd(110) observed by Gentle et al. [4] was due to edge reactions [21,22].

Finally it should be emphasized that palladium-catalyzed benzene formation from acetylene provides an ideal system for Monte Carlo simulations since the states observed in temperature-programmed desorption (TPD) are desorption- and not reaction-rate limited. This means that the surface reaction is sufficiently fast that the simulation does not rely on the use of adjustable kinetic parameters but merely interrogates the nature of the ensembles formed following acetylene adsorption, an essentially statistical process ideally suited for computer simulations.

2. Simulation scheme

Both surface spectroscopic data and the results of theoretical calculations show that acetylene adsorbs on Pd(111) with its C=C axis parallel to the surface on a three-fold hollow site and can adopt three possible orientations relative to the surface [1,8,10,23–25] with the H–C=C–H plane tilted away from the surface normal. Thus, an ensemble of three triangularly related sites can potentially provide a template for benzene formation if all the adsorbed acetylene molecules are correctly oriented with respect to each other. Such a surface template effect has been proposed previously [25,26]. As noted above, benzene is formed by reaction of acetylene and adsorbed C_4H_4 so that the acetylene triads in fact probably consists of a $C_4H_4 + C_2H_2$ ensemble.

The simulation was performed for adsorption on Pd(111) using an hexagonal lattice substrate allowing acetylene to adsorb at a three-fold site in accord with its experimentally determined geometry [10,23–25]. Adjacent sites are blocked for further acetylene adsorption based on the van der Waals radii of the atoms in the molecule, and the excluded sites are depicted in Fig. 1a and forbidden geometries in Fig. 1b where the icons represent rehybridized acetylene with its molecular plane tilted away from the surface normal. Note that no molecular interactions, except for these purely geometrical effects, are included.

A simulation scheme has been adopted as follows:
(i) An adsorption site $S_{i,j}$ is selected at random.
(ii) If it is empty and therefore not directly blocked for adsorption, the neighboring sites are interro-

gated. If the environment permits molecular adsorption, one of its three possible orientations is randomly selected. The environment is again interrogated in order to avoid forbidden configurations (Fig. 1b). If all of these conditions are fulfilled, then the trial is accepted and the molecule allowed to adsorb. Otherwise the trial is rejected and no adsorption occurs.

(iii) After a certain number of trials, all the adsorbed molecules on the lattice are allowed to move merely by jumping to neighboring sites. This event is allowed if the new configuration is not one of the forbidden ones (see (ii)). This procedure was performed every $N^2/36$ trials, for an $N \times N$ lattice, so that N^2 corresponds to the total number of palladium adsorption sites. Typically N is 600.

The process is stopped after a sufficiently large number of trials have been performed that all further attempts to adsorb on the surface fail. This procedure yields a calculated value for the saturation coverage of acetylene on palladium (see below).

Surfaces with intermediate acetylene coverages are prepared by stopping the simulation after a number of adsorption trials and resulting coverage measured just by counting the number of adsorbed acetylene molecules. Various properties of the surface can be examined. For example, the number of ensembles of acetylene molecules that are in the proper hexagonal configuration to form benzene (Fig. 2a) can be calculated. As noted above, an alternative reaction scheme has been proposed in which two adsorbed C_4
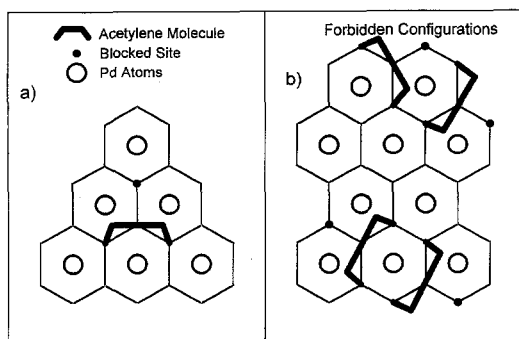

Fig. 1. Schematic diagrams showing (a) sites blocked for subsequent adsorption by a previously adsorbed acetylene molecule (b) unallowed acetylene configurations. Illustrated also in (b) are the blocked sites.
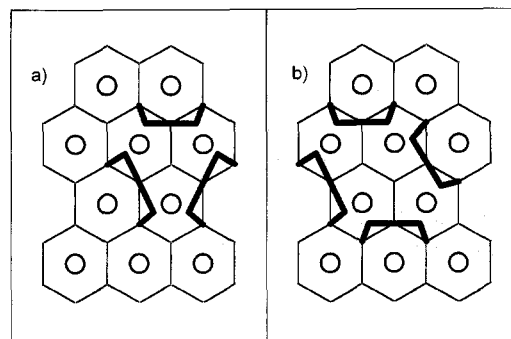

Fig. 2. Ensembles of acetylene adsorbed on Pd(111) that are assumed to lead to (a) benzene formation and (b) cyclooctatetraene formation.

species (formed from four acetylenes) combine to synthesize C_8H_8 which may be sufficiently unstable that it decomposes to yield benzene and acetylene [8,13,14]. Corresponding ensembles of four acetylenes are counted to sample the relative importance of this pathway in the synthesis of benzene (Fig. 2b). The benzene yield measured by counting the $C_4 + C_4$ ensembles assumes that this reaction pathway is as efficient as the $C_2 + C_4$ route. Since dimerization of C_4 species is a $4 + 4$ electron process as opposed to $C_2 + C_4$ coupling which is a $4 + 2$ electron process, it may be less efficient so that the benzene yield calculated for this process represents an upper limit. These and other configurations of interest will be discussed in greater detail below.

Adsorbed oxygen structures are calculated by allowing oxygen atoms to block adjacent sites for acetylene adsorption and oxygen was allowed to adsorb prior to acetylene. The oxygen–oxygen interaction was taken to be a hard "disk" potential of a given radius (three lattice parameters) to obtain the maximum coverage of $\theta_m(O) = 0.25$, as found experimentally [19].

All calculations were carried out using SUNSparc minicomputers and the programs were written in C + +.

3. Results

3.1. Benzene desorption yield on Pd(111)

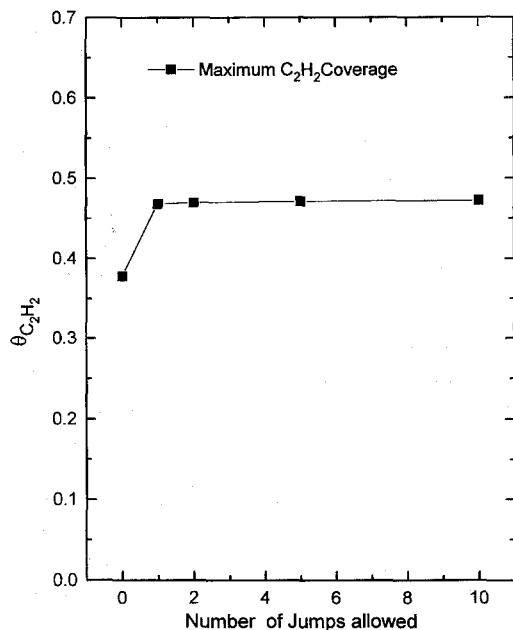The saturation acetylene coverage on Pd(111) was calculated as described above, but allowing no sub-

Fig. 3. Calculated saturation coverage of acetylene on Pd(111) plotted versus the number of diffusion steps allowed for each molecule (■).
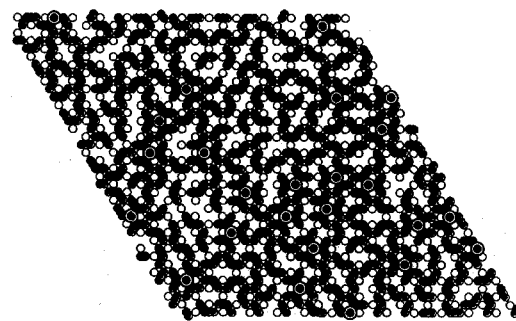

Fig. 4. Snapshot of a saturated acetylene overlayer on Pd(111). Substrate palladium atoms are indicated by open circles and the dark icons represent rehybridized, adsorbed acetylene with its H–C=C–H plane tilted away from the surface normal. Typical triplets of acetylene correctly oriented for form benzene are marked (⊙).

sequent diffusion. This leads to a saturation acetylene coverage of 0.38 compared with an experimentally found value of 0.46 [1]. It has been shown, however, that acetylene adsorbs onto Pd(111) at ∼ 200 K via precursor state kinetics [1] implying that there is some mobility of the adsorbed layer during adsorption. Allowing some surface diffusion after the acetylene has adsorbed (see Section 2) increases the amount of acetylene that can be accommodated. Shown in Fig. 3 is the saturation coverage of acetylene on the (111) surface plotted as a function of the number of diffusion steps that were allowed for each acetylene molecule (■) (see Section 2). The saturation coverage increases rapidly merely by allowing the molecules to jump once. As the number of diffusion steps increases, a further small increase in saturation coverage is noted which rapidly reaches an asymptotic value when four or more jumps are allowed. The saturation coverage at this point is 0.469; in extremely good agreement with that found experimentally [1]. Shown in Fig. 4 is a snapshot of a resulting acetylene-saturated surface. The open circles represent the palladium sub-

strate atoms and the acetylene molecules are depicted by five black circles to represent the tilted, rehybridized geometry of the adsorbed acetylene found experimentally and predicted theoretically [10,23–25].

Fig. 5 reproduces a typical set of temperature-programmed desorption spectra obtained following various exposures of acetylene to a Pd(111) surface at a
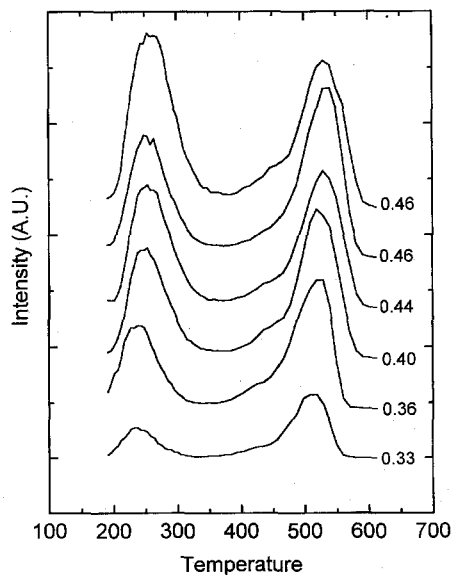

Fig. 5. Typical benzene thermal desorption spectra following acetylene adsorption on Pd(111). Acetylene coverages are marked adjacent to their corresponding spectra.
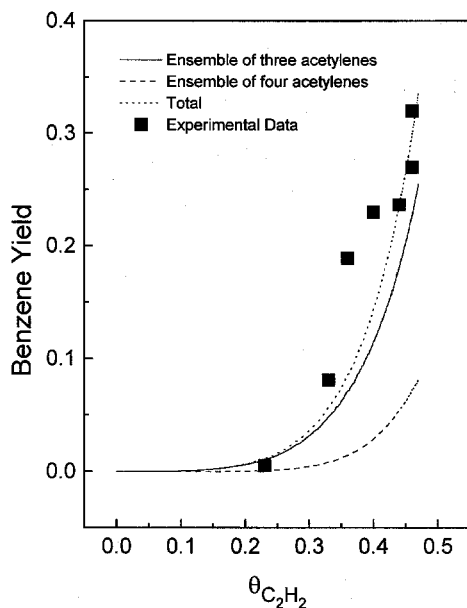
Fig. 6. Plot of the experimental total integrated desorption yield from Pd(111) as a function of acetylene coverage (■). Plotted also onto these data is the benzene yield calculated by assuming that a correctly oriented triplet of acetylene molecules is required for benzene formation (————) and by assuming that two cofacial C_4 species are needed (------). Plotted also is the sum of these two yields (· · · · · ·).

substrate temperature of ~ 190 K taken from Ref. [1]. Corresponding acetylene coverages are marked adjacent to each spectrum which display the distinct two-peaked structure alluded to above where the low-temperature state has been assigned to the desorption of a sterically crowded benzene from the surface [16] and the high-temperature state to the evolution of flat-lying benzene [17]. The total benzene yield is proportional to the integrated area under the thermal desorption trace. It has been shown, by measuring the C 1s X-ray photoelectron peak intensity of a saturated acetylene overlayer on Pd(111) as a function of sample temperature, that approximately $32 \pm 3\%$ of the layer converts to benzene [1,10]. Shown in Fig. 6 is the total benzene yield (normalized to a 32% conversion) for the saturated overlayer, as a function of acetylene coverage (■). As outlined above, it has been proposed that acetylene is formed by the reaction of a C_4 with an adsorbed acetylene molecule or alternatively by reaction of two C_4 species to form cyclooctatetraene

which decomposes to form benzene and leave acetylene. Both of these reactions are analogous to Diels–Alder cycloadditions and it is postulated that one of the roles played by the palladium substrate is to correctly orient the adsorbed molecules to allow such cycloaddition reactions to proceed. Clearly a three-fold (111) surface has the correct symmetry for orienting acetylene molecules to allow overlap between a C_4 and adsorbed acetylene [26,27]. Correctly oriented ensembles of three acetylene molecules, which are depicted in Fig. 2a, are identified on the snapshot in Fig. 4 (○). The number of these ensembles is plotted as a function of the acetylene coverage on the experimental data of Fig. 6 (————) and agrees very well with the experimentally measured value, not only in the general shape of the curve, but also it quantitatively predicts the total benzene yield found experimentally. It is interesting to note that the acetylene overlayer exhibits a $\sqrt{3} \times \sqrt{3}$ R30° LEED pattern at a coverage of 0.33 [1] whereas the simulated overlayer structures (see for example Fig. 4) show no apparent evidence of order. However, 150×150 lattices of the acetylene overlayer were simulated using the protocols outlined above and photographed onto 35 mm film. The diffraction properties were interrogated using a helium/neon laser and the apparently randomly ordered overlayer exhibited a 1×1 diffraction pattern. Clearly, there is sufficient orientational correlation between neighboring adsorbates to cause diffraction [28]. The simulation scheme is being modified to explore the formation of other LEED structures without compromising the kinetics results. For example, it has been assumed for simplicity in the simulation that hcp and fcc three-fold sites have identical reactivities so that, for example, the effect of changing the adsorption probabilities onto these sites is being explored.

It has also been found that low coverages of benzene on clean Pd(111) thermally decompose to yield hydrogen at ~ 580 K [17]. This peak is absent for benzene reactively formed from acetylene [1] so that this pathway is suppressed in this case. Here, however, reactively formed benzene is surrounded by decomposition products from acetylene that has not converted to benzene which may effectively suppress decomposition [17,18]. The number of corresponding correctly oriented ensembles of four

acetylene molecules depicted in Fig. 2b are used to calculate the benzene yield due to the formation and decomposition of C_8H_8, and the result is also shown in Figure 6 (------) along with the total amount of benzene arising from both sources ($\cdot$ $\cdot$ $\cdot$ $\cdot$ $\cdot$). It is clear that the benzene arising from the latter route (i.e., cyclooctatetraene decomposition) cannot explain the efficiency of the reaction alone. The total benzene formed by both routes results in a slightly improved agreement with experiment, where the standard deviation between experiment and theory decreases from 0.032 for benzene formation via three acetylenes (ensemble in Fig. 2a), to 0.0225 for benzene formed by the two routes (Figs. 2a and 2b). However, the improvement in the agreement is somewhat marginal and does not allow us to say definitively whether C_8 formation contributes to the formation of benzene on Pd(111).

3.2. Desorption peak intensity ratio on Pd(111)

It has been proposed that the low-temperature (~ 280 K) benzene desorption state arises from benzene that is sterically crowded on Pd(111) [16,17,18] whereas the high-temperature (~ 520 K) state is due to benzene adsorbed on a sufficiently large ensemble that it can lay flat. Plotted in Figs. 7 and 8 is the experimentally measured ratio of the integrated intensity of the low-temperature (280 K) desorption state to that of the high-temperature (529 K) state ($\bullet$) as a function of acetylene coverage. Benzene is formed on the surface surrounded by unreacted acetylene molecules, and the cartoons in Fig. 9 show all possible acetylene environments around a reactively formed benzene. These can either be oriented tangentially to the benzene ring (see, for example, Fig. 9b) or with the acetylenes oriented at 120° in this direction. The adsorbed molecules shown in Fig. 9 are represented by their van der Waals radii, and this therefore suggests that reactively formed benzene is not prevented from laying flat by adjacent, tangentially adsorbed acetylene. Accordingly, adjacent acetylenes with this orientation are *not* counted as neighbors as far as steric crowding is concerned so that configurations 9a and 9b are taking to have *no* nearest-neighbor acetylenes. The number of these configurations can also be counted and is designated $n(0)$. Clearly an adsorbed benzene molecule sur-
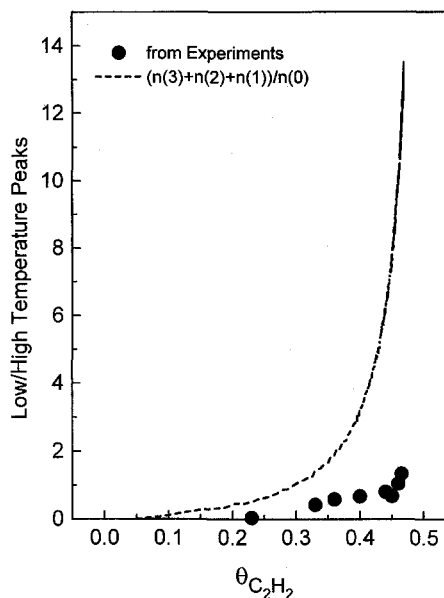

Fig. 7. Plot of the ratio of the integrated intensity of the low-temperature (280 K) benzene desorption state to the high-temperature (520 K) state ($\bullet$). Plotted also onto the results is the calculated ratio $(n(1)+ n(2)+ n(3))/n(0)$ (see text) (------).

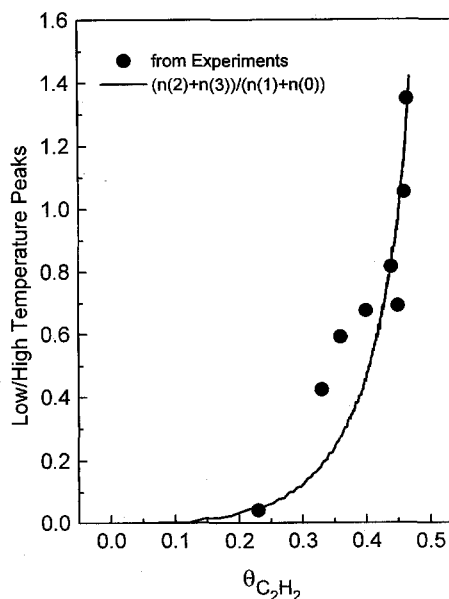

Fig. 8. Plot of the ratio of the integrated intensity of the low-temperature (280 K) benzene desorption state to the high-temperature (520 K) state ($\bullet$). Plotted also onto the results is the calculated ratio $(n(2)+ n(3))/(n(0)+ n(1))$ (------). Note the correspondence between experiment and simulation (see text).

rounded by three acetylene molecules (9(e)) is drastically sterically hindered. Similarly, the configuration 9d is unlikely to allow the reactively formed benzene to lay flat. Careful examination of the space available for a benzene molecule with *one* adjacent acetylene (Fig. 8c) suggests that there is insufficient space for it to be accommodated parallel to the surface. This implies that the ratio of the number of benzene molecules with either one, two or three adjacent acetylene molecules to the number of benzenes with no neighbors $(n(3) + n(2) + n(1))/n(0)$ should reflect the intensity ratio of the low- and high-temperature desorption states. The results of this calculation are plotted also in Fig. 7 (------) and predicts that the majority of the reactively formed benzene should desorb at 280 K, in complete contrast to experimental observations. If it is assumed, however, that reactively formed benzene having only one nearest neighbor can, in fact, lay flat, the corresponding intensity ratio of the low-to-high-temperature peak is now given by $n(3) + n(2))/(n(1) + n(0)$. This ratio is compared with the experimental values in Fig. 8 (———) where now the agreement is good.

This model assumes that the surface remains static during the thermal desorption sweep, particularly in the range of temperatures when the sterically crowded benzene desorbs (from 150–300 K). Adsorbed acetylene, however, converts to vinylidene over just this temperature range [15]. Since vinylidene occupies significantly less space on the surface than acetylene [1], conversion of acetylene to vinylidene may relieve surface crowding and allow benzene that is initially formed in a crowded environment to lay flat. The acetylene to vinylidene conversion kinetics have been measured [29], and using these results the remaining acetylene coverage during low-temperature benzene desorption is plotted in Fig. 10 (■)
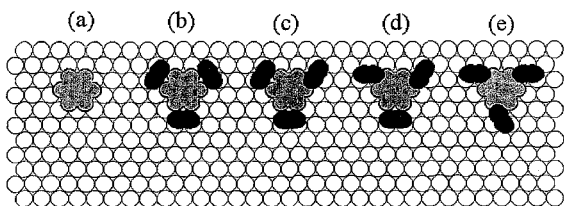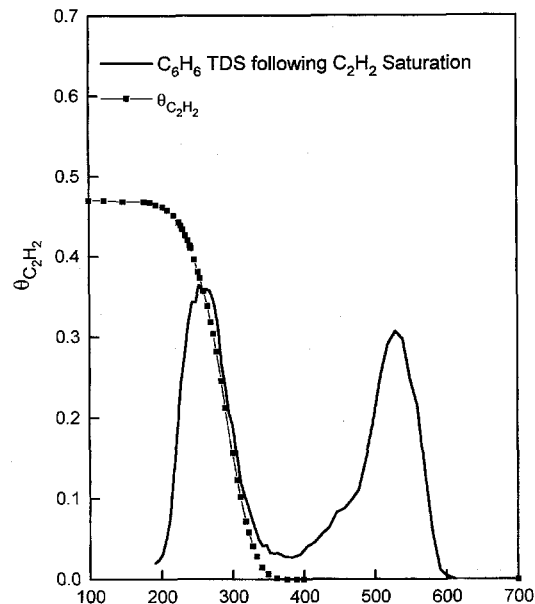

Fig. 10. Remaining acetylene coverage as a function of temperature due to conversion to vinylidene (■) compared with the low-temperature benzene desorption profile at acetylene saturation coverage (———).

compared to the benzene desorption profile (———). This result implies an alternative scenario where the majority ($\sim 90\%$) of the reactively formed benzene initially adopts a tilted configuration, but lays flat as the temperature is raised as crowding is relieved by acetylene to vinylidene conversion. An alternative possibility is that some acetylene desorbs from the surface to relieve crowding. However, very little acetylene desorption is found in temperature-programmed spectroscopy [1]. These processes are being further investigated.

3.3. Benzene formation on oxygen-covered Pd(111)

In order to further test the simulation scheme and algorithms, *exactly identical* strategies have been applied to calculating the total benzene yield in the TPD spectra for acetylene adsorbed onto oxygen-covered Pd(111) using the experimental results of Ormerod et al. [19]. The benzene yield decreases substantially as a function of increasing oxygen coverage but the variation cannot be rationalized just on the basis of a decrease in the amount of acetylene
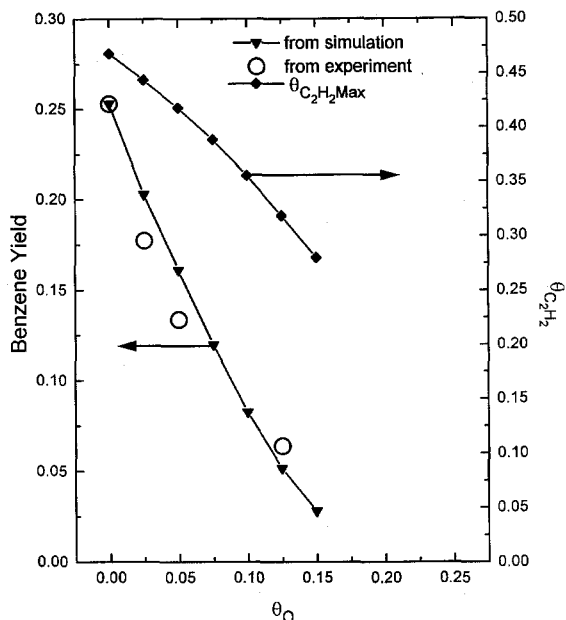

Fig. 9. Schematic figure showing various acetylene environments around benzenes reactively formed from acetylene on Pd(111).

Fig. 11. Benzene desorption yield following acetylene adsorption on oxygen-covered Pd(111) plotted as a function of θ_O where θ_O refers to the relative oxygen coverage ($\bigcirc$). Plotted also is the predicted acetylene coverage ($\blacklozenge$) and the benzene desorption yield ($\blacktriangledown$) both as a function of oxygen coverage.

adsorbed. Fig. 11 displays the experimentally found variation in the amount of benzene formed in TPD on oxygen-covered Pd(111) as a function of the oxygen coverage (θ_O) (taken from the data in Ref. [19]; $\bigcirc$). Plotted also onto this figure is the saturation acetylene coverage calculated in the same way as was done for clean Pd(111) as a function of $\theta(O)$ ($\blacklozenge$). The acetylene coverage *does* decrease with increasing oxygen coverage but more slowly than would account for the decrease in benzene formation. However, also plotted onto these data is the benzene yield as a function of oxygen coverage calculated from the number of acetylene triads correctly oriented to form benzene (depicted in Fig. 2a ($\blacktriangledown$)). This agrees well with the experimental data further confirming the validity of the simulation strategy.

3.4. Structure sensitivity of benzene formation on palladium in temperature-programmed desorption

Acetylene formation is structure sensitive on palladium both in ultra-high vacuum (where the ben-

zene yield following saturation of the surface with acetylene varies strongly with crystal face) as well as at high pressures in the catalytic reaction [2,4,20,22]. The variation in benzene TPD yield is not surprising in view of the geometrical constraints and template effect required to successfully rationalize benzene formation on Pd(111) [26,27]. The results presented here indicate that the hexagonal symmetry of Pd(111) appropriately orients the adsorbed acetylene molecules to allow them to react to form benzene. Clearly, the two- or four-fold symmetries of Pd(110) and Pd(100) respectively cannot similarly correctly orient adsorbed acetylene. This notion provides a simple first-order rationalization of the lower yield of benzene in these cases. It is, however, more likely that these surface will orient acetylene to form cyclooctatetraene [8,13,14]. It would therefore a priori be expected that this would be preferred benzene formation route on these surfaces. The simulation scheme described above has been applied to examining the structure sensitivity of benzene formation in temperature-programmed desorption on Pd(100) and, for Pd(110), using an acetylene adsorption geometry suggested by Yoshinobu [21]. Fig. 12 displays cartoons of the proposed ensembles to the formation of benzene via C_8 intermediates on Pd(100) and Pd(110)

Fig. 13 displays histograms showing the relative experimental benzene yield in temperature-programmed desorption on various palladium surfaces taken from reference [4,5,21,22] where the yield on Pd(111) has been normalized to 100%. For the purposes of calculation, acetylene is allowed to adsorb on the Pd(100) surface at bridge sites which predicts a saturation acetylene coverages of 0.47. Note that
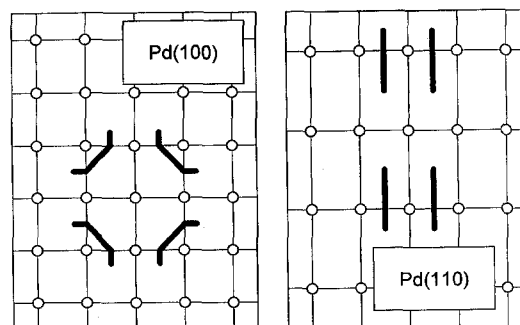

Fig. 12. Cartoons of the acetylene ensembles on Pd(110) and Pd(100) that may lead to C_8 formation, (see text).
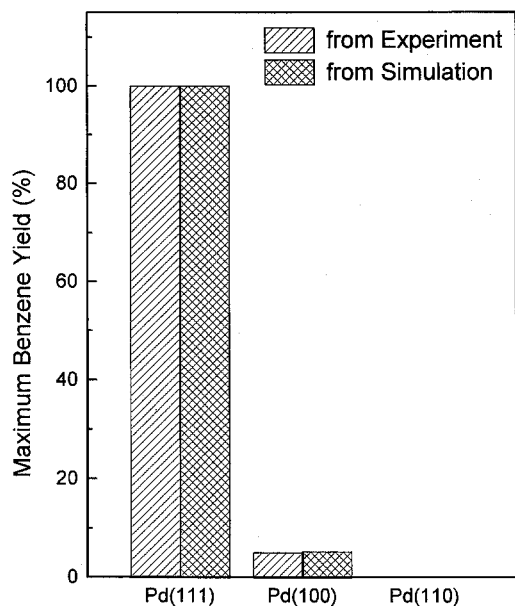
Fig. 13. Histogram displaying the relative experimental yields from Pd(111), Pd(110) and Pd(100) after saturating these surfaces with acetylene compared with the results of a simulation (see text).

there are no ensembles with three correctly oriented acetylene molecules, as expected, and the ensembles of four acetylene molecules proposed to lead to cyclooctatetraene and ultimately benzene formation are depicted in Fig. 12a. The total simulated benzene yield due to reaction of these ensembles on Pd(100) are shown plotted in histogram form and compared with the experimental results in Fig. 13 and the agreement between the two values is very good. This result is therefore in accord with the view that the relative orientations of the adsorbed acetylene molecules is crucial in determining the total amount of benzene adsorbed on the surface and that reaction on Pd(100) likely proceeds via the formation of C_8H_8 which decomposes to form benzene. Further refinement of the model will be possible once the correct adsorption geometries for acetylene on this surface are known.

The corresponding geometry for acetylene adsorbed on Pd(110) would probably result in the formation of two C_4 species too far apart to react

rapidly to form benzene, since the nearest C–C distance is 4.8 Å (Fig. 12b). This would therefore suggest that the Pd(110) surface should be completely inactive for benzene formation in agreement with Yoshinobu et al. [21] and this result is shown for comparison on Fig. 13. Note that these simulation neglect any changes in the reactivity of the surface for different exposed crystal faces. It is interesting to note, however, the Cu(110) is rather active for the synthesis of benzene from acetylene [30] implying that similar geometrical constraints may not be as important in this case.

4. Conclusions

The total amount of benzene formed on Pd(111) as a function of acetylene coverage can be rationalized by assuming that when three acetylene molecules are correctly oriented on the surface they can react to form benzene; the substrate forms a template for benzene synthesis. A small amount of benzene formation is also expected from a C_8 precursor but the experimental results are not sufficiently accurate to say definitively whether this route actually contributes to benzene formation on Pd(111). The relative yield of benzene at low temperature (in the 280 K desorption state) is calculated by assuming that any benzene that is formed on the surface with two or more acetylene neighbors is sterically crowded and that the yield of benzene at high temperature (~ 520 K) is due to benzene with only one or less adjacent acetylenes and can lay flat. This procedure yields good agreement with experiment. However, this model assumes a static surface configuration during the desorption sweep, whereas, in fact, adsorbed acetylene converts to vinylidene over this temperature range.

These ideas can also be directly applied to correctly rationalizing the total benzene yield from oxygen-covered Pd(111) as a function of oxygen coverage without any further assumptions. Finally, simulation of the benzene yields as a function of surface structure, assuming that on Pd(100) reaction proceeds via cyclooctatetraene formation, gives good agreement with the experimental data also using identical assumptions as were used to calculate the properties of Pd(111).

Acknowledgements

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