# Surface Structure and Reactivity in the Cyclization of Acetylene to Benzene with Pd Overlayers and Pd/Au Surface Alloys on Au{111}

## Christopher J. Baddeley,<sup>†</sup> R. Mark Ormerod,<sup>‡</sup> Andrew W. Stephenson,<sup>†</sup> and Richard M. Lambert<sup>\*,†</sup>

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW U.K., and Department of Chemistry, University of Keele, Keele, Staffordshire, ST5 5BG U.K.

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The catalytic activity of Pd overlayers and Pd/Au surface alloys on Au{111} toward acetylene cyclization has been studied as a function of surface morphology and composition using LEED, XP and Auger spectroscopy, temperature-programmed reaction, and STM. At 300 K pseudomorphic islands of Pd nucleate and grow uniformly from the partial surface dislocations of the Au{111} herringbone reconstruction. Even 0.1 monolayer (ML) Pd loadings are catalytically effective, and activity scales linearly with coverage by these monolayer Pd islands up to  $\sim 0.6$  ML. Beyond this point, concurrent growth of higher layers leads to a roughened surface, the appearance of new binding sites for reactively formed benzene, and ultimately the suppression of all cyclization activity, thus demonstrating the extreme structure sensitivity of the system. Annealing rough Pd films restores activity and can be used to induce surface alloy formation. Core-level spectra indicate that electronic perturbation of Pd by Au is insignificant and the Au/Pd surface alloy behaves as a very effective catalyst. The principal effect of Au atoms at the surface is to modify the ensembles available for reactant and product adsorption, influencing conversion of the former and strongly enhancing the desorption rate of the latter. Mechanistic implications of these findings are discussed, and their relevance to an understanding of the cyclization behaviour of supported Pd and Au/Pd catalysts operated at atmospheric pressure is indicated.

#### Introduction

Acetylene coupling reactions on Pd surfaces constitute an interesting class of processes which, depending on the conditions, can yield a variety of linear and cyclic products including heterocycles.<sup>1-3</sup> They display very close similarities with alkyne coupling reactions catalysed by transition metal cluster compounds and provide a most striking example of the cluster/ extended metal surface analogy. Furthermore, they can be carried out over dispersed Pd catalysts at atmospheric pressure.<sup>4</sup>

The key process involves formation of a C<sub>4</sub>H<sub>4</sub> metallocycle common intermediate which then reacts further: benzene formation, the prototype reaction, involves addition of a third acetylene molecule. Studies, including theoretical investigations, covering many structural, kinetic, and mechanistic aspects have appeared,<sup>5-11</sup> and the topic has been recently reviewed.<sup>12,13</sup> Benzene formation in particular exhibits very pronounced sensitivity to the surface crystallography, Pd{111} being by far the most effective crystal face.<sup>14,15</sup> This suggests that alloying with a second metal could be a very effective means of selectivity control, an expectation borne out by results obtained with novel Au/Pd<sup>16</sup> and Sn/Pd<sup>17</sup> dispersed catalysts. Here we report the results of a structural and catalytic study in which Au{111}/Pd was used as a model catalyst. A combination of LEED, XPS, STM, and temperature-programmed reaction (TPR) data yields useful insight into the surface chemistry of the bimetallic system and the properties of closely related Au/Pd practical catalysts. Some structural information on Au{111}/ Pd has already been published by Koel et al.<sup>18</sup> using LEIS, and more recently by ourselves.<sup>19</sup> The latter included results of a detailed TLEED/XPS/Auger investigation in which the structure and stability of pseudomorphic Pd overlayers and of an ordered Au/Pd surface alloy were determined: the catalytic behavior of both is described here. Morphology of the pure Pd films profoundly affects their catalytic efficacy and intermixing with Au drastically accelerates the desorption of reactively formed benzene.

#### **Experimental Section**

Three different UHV chambers were used, two of which have been described previously.<sup>20,21</sup> Temperature-programmed reaction (TPR) experiments were carried out in the chamber 1 using a collimated, multiplexed quadrupole mass spectrometer; this chamber was also equipped with a LEED/AES system. Chamber 2 incorporated a VSW HA-100 XPS instrument (MG Ka radiation). STM observations were performed in a third chamber which housed an Omicron STM-1 microscope and LEED/AES facilities. In all three chambers, Pd deposition was achieved at an ambient pressure of  $< 2 \times 10^{-10}$  Torr using resistively heated, collimated evaporation sources. Palladium uptake was monitored by following the Pd MNN (330 eV) and Au NOO (69 eV) Auger transitions, the latter providing considerable sensitivity to the presence of overlying Pd. Between experiments involving different Pd loadings, the Au sample was cleaned by argon ion bombardment ( $\sim 5 \mu A$ , 500 V) and annealed to ~850 K to restore a clean, well-ordered surface as judged by LEED/Auger spectroscopy or STM/Auger spectroscopy.

In chambers 1 and 2, Pd deposition was carried out at <170 K after which the sample was annealed to the desired temperature (up to 550 K) for 5 min followed by cooling to <170 K prior to acetylene adsorption. Research grade acetylene was further purified by cooling to  $\sim$ 200 K to remove possible traces of contamination by benzene before admission to the sample surface by means of a quartz capillary array doser. A saturation

<sup>&</sup>lt;sup>†</sup> University of Cambridge.

<sup>&</sup>lt;sup>‡</sup> University of Keele.

<sup>\*</sup> Corresponding author.

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dose (6 layers) of acetylene was used in every TPR experiment with a heating rate of ~8 K s<sup>-1</sup>. Pd deposition in the STM apparatus was carried out at room temperature. Quoted Pd coverages are based on the attenuation of the Au (69 eV) Auger transition assuming an inelastic mean free path of 69 eV electrons of 4 Å, a figure used previously for calculations using similar Au/Pd systems.<sup>22</sup> In the STM experiments coverages in the submonolayer regime were calculated directly from the images by dividing the total Pd island area by the total image area.

#### **Results and Discussion**

Electronic Modification of Pd Overlayers by Au. Pd deposition resulted in a small ( $\sim 0.2 \text{ eV}$ ) increase in the observed Au 4f BE consistent with the known surface core level shift of pure Au;<sup>23</sup> in accord with this, the effect was reversed on annealing to progressively higher temperatures which resulted in intermixing and reappearance of Au atoms at the surface. Furthermore, the Pd 3d BE of submonolayer films was undetectably different from that of 6ML films, in agreement with results obtained by Koel et al.<sup>18</sup> This is very different from the behavior of monolayer Pd films on W and Ta substrates<sup>24</sup> where Pd 3d BE shifts of >0.5 eV are accompanied by substantial changes in CO chemisorption properties. Thus both the Au and Pd data indicate minimal electronic perturbation of palladium by gold, so as a first approximation it seems natural to interpret changes in chemical behavior mainly in terms of geometric or ensemble effects.

Structure and Catalytic Activity of Submonolayer Pd Films. For the temperature-programmed reaction (TPR) experiments Pd deposition was carried out at 170 K, followed in most cases by various annealing treatments (the sample was maintained at the required temperature for 5 min), prior to cooling and acetylene chemisorption at 170 K. This procedure was followed (i) to investigate the reactive properties of poorly ordered films and (ii) to minimize the extent of Au/Pd intermixing at the start of an experiment. STM images were acquired at room temperature, in some cases after appropriate thermal treatment of the sample.

Figure 1a shows benzene TPR data obtained after acetylene adsorption on a series of Pd films (0.1 to  $\sim$ 0.1 ML) deposited at 200 K and preannealed to 300 K. Our LEED studies<sup>18</sup> indicate that this procedure leads to formation of a pseudomorphic Pd overlayer on Au(111). A striking feature of Figure 1 is that even a 0.1 ML Pd film is active for benzene production and that the benzene is evolved in two peaks  $(\alpha, \gamma)$  in a manner which closely parallels the behavior of clean Pd(111). A considerable amount of earlier work<sup>25</sup> indicates that these two peaks are due to the desorption rate-limited evolution of benzene from tilted ( $\alpha$ , lower temperature) and flat-lying ( $\gamma$ , higher temperature) states, respectively. Up to at least 0.5 ML the total benzene yield scales linearly with Pd coverage, and there is a systematic shift of both high- and low-temperature peaks toward the values characteristic of pure Pd(111), which are eventually attained in the 0.4 ML case. The Pd(111)-like behavior exhibited by a submonolayer Pd film confirms the expectation from XPS that the electronic structure of the overlayer is not greatly perturbed by the Au substrate. The spectrum from the 1 ML Pd overlayer shows a third feature ( $\beta$ ) at intermediate temperature; it has been proposed<sup>15</sup> that this is associated with benzene desorption from defect or non-{111} like Pd sites.

The corresponding STM data obtained for films deposited at 300 K are revealing and serve to demonstrate directly some of the essential features of acetylene cyclization catalysis by Pd



Figure 1. TPR data for acetylene to benzene conversion as a function of Pd loading. Pd deposited at  $\sim 170$  K, sample annealed to 300 K, cooled to  $\sim 170$  K and dosed with 6 layers of acetylene: (a, top) submonolayer coverages; (b, bottom) coverages >1 ML.

overlayers. Figure 2 shows a 0.07 ML Pd deposit: it is apparent that islands of Pd nucleate at the partial surface dislocations of the Au{111} herringbone reconstruction. (Such behavior has been reported previously for <sup>26</sup>Fe, <sup>27</sup>Co, and <sup>28</sup>Ni overgrowths on Au{111} where there is also a substantial mismatch between overlayer and substrate; Ag, with a small mismatch, behaves very differently.<sup>29</sup> Close inspection of the images indicates that the nucleation tends to occur preferentially on the fcc domains.<sup>30,31</sup> Recent STM results<sup>31</sup> have revealed that the Pd islands are close packed with 3-fold symmetry. It is important to note that the island size ( $\sim 30$  Å) is sufficiently large to accommodate flat-lying reactively formed benzene molecules, although many of these will lie at sites close to the island edges where their bonding is likely to be perturbed. For example, we can illustrate this by noting that on such a  $\sim 30$  Å island a full monolayer of flat-lying benzene would contain  $\sim 15$ molecules,  $\sim 60\%$  of which would lie at such perturbed edge sites. This could account for the progressive evolution with coverage of the  $\alpha$  and  $\gamma$  TPR peak temperatures towards the characteristic Pd{111} values. The relatively well-resolved TPR peaks imply that one is dealing with a rather homogeneous array of Pd entities, and the STM data confirm that this is indeed the



**Figure 2.** 0.07 ML Pd deposited on  $(23 \times \sqrt{3})$ Au{111} at 300 K. The Pd islands nucleate at the "elbows" of the "herringbone" structure where partial surface dislocations are present. Many of the larger islands have sharp edges following close packed directions in the Au{111} substrate (1000 Å × 1000 Å × 2.9 Å,  $V_t = 0.5$  V,  $I_t = 1.0$  nA).



**Figure 3.** 0.7 ML Pd deposited on  $(23 \times \sqrt{3})$ Au{111} at 300 K. Further growth of the Pd islands reveals well defined edges that follow close-packed directions in the Au{111} substrate. Some second layer islands also show well-defined edges which alludes to the ordered nature of the Pd overlayers (1500 Å × 1500 Å × 4.9 Å,  $V_t = 2$  V,  $I_t = 1.0$  nA).

case (Figure 2). The appearance of the  $\beta$  TPR peak at around the monolayer point (Figure 1) is interesting and the STM images powerfully confirm our earlier hypothesis that this feature is associated with step sites and a roughened Pd morphology resulting from onset of second layer growth before completion of the first layer. This morphology is clearly apparent in Figure 3 which shows the structure of a 0.7 ML deposit: it is clear that the surface contains an appreciable fraction of non-{111} Pd sites.

Figure 4 shows the integrated benzene yield for 300 K annealed Pd films in the range 0-2.5 ML and Figure 1b shows typical TPR spectra obtained for coverages above 1 ML. The



Figure 4. Benzene yield as a function of Pd overlayer thickness, derived from the data in Figure 1.



**Figure 5.** 3 ML Pd deposited at 300 K on  $(22 \times \sqrt{3})$ Au{111}. Thicker layers of Pd display island upon island growth patterns (1000 Å × 1000 Å × 17.7 Å,  $V_t = 1.5$  V,  $I_t = 0.5$  nA).

very pronounced maximum in benzene production followed by a strong decrease for >1 ML Pd is interesting, and at first sight surprising: leveling off to a limiting level of activity might have been expected. (The suppression of the  $\alpha$  peak which accompanies this reflects the decreased level of cyclization: the  $\alpha$  peak is characteristic of a relatively high level of conversion.)-

The decrease in activity following the deposition of a Pd monolayer is unexpected on the basis of perfect pseudomorphic growth. Indeed it would be reasonable to assume that perfect pseudomorphic growth would result in the benzene yield reaching saturation once the uppermost surface layers consisted of pure Pd. However, the 5% lattice mismatch between Pd and Au would be expected to arrest pseudomorphic growth at a relatively early stage. This is in accord with the STM image shown in Figure 5 which is for a 3.0 ML Pd deposit at 300 K. The film has growth by simultaneous evolution of a number of layers, resulting in a rough morphology and a reduction in availability of ideal {111} adsorption sites. In line with this, the sample exhibits a diffuse  $(1 \times 1)$  LEED pattern. It is known that acetylene cyclisation is very sensitive to the details of Pd surface structure<sup>14,15</sup> with the {111} surface being by far the most effective. The loss of catalytic activity despite increased Pd film thickness is therefore understandable.

The above interpretation is confirmed by data obtained after annealing such rough multilayer films before acetylene adsorpCyclization of Acetylene to Benzene



**Figure 6.** TPR data for acetylene to benzene conversion from a 3.7 ML Pd film deposited at  $\sim$ 170 K as a function of annealing temperature. Following annealing treatment the sample was cooled to  $\sim$ 170 K and dosed with 6 layers of acetylene.



**Figure 7.** Atomic resolution image of the ordered Pd<sub>2</sub>Au alloy formed after annealing to 525 K. The 3-fold symmetry of the alloy surface is slightly distorted due to thermal drift while scanning (60 Å × 60 Å × 1.2 Å,  $V_t = -0.7$  mV,  $I_t = 0.5$  nA).

tion and reaction: their efficacy for cyclization is greatly enhanced. Figure 6 shows the benzene TPR results obtained with 3.7 ML Pd films *preannealed* to 400 and 550 K. It is apparent that 400 K annealing causes an increase in benzene yield compared to the almost inactive 300 K annealed film. This treatment induces a higher degree of perfection in the initially rough film (confirmed by LEED) resulting in benzene desorption kinetics almost identical with those observed with a Pd{111} single crystal.<sup>1</sup> 550 K annealing results in formation of a Pdrich ( $\sqrt{3} \times \sqrt{3}$ )R30° surface alloy<sup>19</sup> and Figure 7 shows an atomically resolved STM image of the alloy surface. Though it was not possible to distinguish the Pd and Au atoms under our imaging conditions, it is clear that the alloy surface is well ordered and possesses fcc {111}-like symmetry.

In this regard it is noteworthy that the model system yields results which permit us to rationalize the acetylene cyclization



**Figure 8.** TPR data for acetylene to benzene conversion from a 1.3 ML Pd film deposited at  $\sim$ 170 K as a function of annealing temperature. Following annealing treatment the sample was cooled to  $\sim$ 170 K and dosed with 6 layers of acetylene.

activity of dispersed Pd catalysts operated at atmospheric pressure.<sup>4</sup> For a given metal loading such catalysts exhibit greater activity when composed of large Pd particles—the opposite of normal expectations. This must reflect the increased proportion of {111} planes at the surfaces of large particles.

Effects of Au/Pd Intermixing. The high bulk miscibility of Au and Pd inevitably results in intermixing at some sufficiently high temperature for overlayer systems of the type studied here. We have already reported results of a detailed TLEED/XPS/Auger study of Au{111}/Pd19 which included a structure determination of the Pd2Au ordered surface alloy phase that forms under suitable conditions. It was concluded that Au/ Pd intermixing was negligibly slow at 300 K, appreciable at 400 K, and rapid above 550 K; this was somewhat at variance with the results of a LEIS investigation<sup>18</sup> which suggested that intermixing is already appreciable at 300 K. The present STM results indicate a possible explanation for this apparent discrepancy. Figures 2 and 3 strongly suggest that in the monolayer regime Pd is confined to islands at the surface and that second layer growth commences before completion of the first layer. An Au signal would therefore persist in the ion scattering spectrum without any intermixing having occurred.

The effects of preannealing on the activity of a 1.3 ML Pd film are illustrated in Figure 8. The roughest film, deposited at 200 K and not subjected to preannealing, shows the lowest activity with benzene desorption occurring from tilted ( $\alpha$ ), flatlying ( $\gamma$ ), and defect or step site states ( $\beta$ ). Slight preannealing (250 K) improves conversion and preannealing to 400 K generates19 a well-ordered overlayer (LEED) whose behavior is essentially identical to that of a Pd{111} single-crystal surface (1). 450 K pretreatment results in formation of the  $(\sqrt{3} \times \sqrt{3})$ -R30° Pd<sub>2</sub>Au surface alloy,<sup>19</sup> and this alloy is at least as active as the pure Pd film: essentially all the benzene is now desorbed from the low-temperature state. Several points are worth making in this respect. (i) Recent cluster calculations<sup>32</sup> indicate that acetylene to benzene conversion on mixed Au/Pd clusters is energetically almost as favorable as it is on pure Pd clusters. (ii) These calculations also show that benzene is more weakly chemisorbed on the mixed cluster, and as might be expected (iii) the greater ease with which benzene can be desorbed from the alloy surface and the (likely) reduced degree of decomposi-



Figure 9. TPR data for acetylene to benzene conversion as a function of Pd loading. Pd deposited at  $\sim$ 170 K, sample annealed to 500 K, cooled to  $\sim$ 170 K, and dosed with 6 layers of acetylene.



Figure 10. Benzene yield as a function of Pd overlayer thickness, derived from the data in Figure 9.

tion of reactant and product molecules provides a natural explanation for the observed enhanced efficiency of Au/Pd dispersed alloy catalysts relative to their pure Pd counterparts.<sup>16</sup> Higher temperatures result in extensive intermixing, loss of Pd from surface sites, and an overall reduction in activity; the formation of flat-lying benzene continues to be inhibited on the Au-enriched surface, as would be expected. This general pattern of behavior was also observed for thicker Pd deposits, the principal difference being that somewhat higher temperatures were required to induce the effects due to ordering and intermixing, as described above. Figure 9 shows results similar to those given in Figure 1 except that a much higher preannealing temperature was used in every case-500 K as opposed to 300 K. This is known to induce essentially complete alloying of the  $\sim 0.5$ , 1, 2, and 4 ML Pd films,<sup>19</sup> and the present results show that only  $\alpha$  benzene is produced as a consequence. However, the TPR fingerprint of the thickest film (~6 ML) clearly indicates that it retains a Pd{111}-like surface after this annealing procedure. The integrated benzene yield as a function of Pd loading derived from the results in Figure 9 plotted is plotted in Figure 10. The ordinate scale is directly comparable with that used in Figure 4. It is at once apparent that the best alloy film ( $\sim$ 3 ML Pd + 500 K)<sup>19</sup> is a very much better catalyst than the best pseudomorphic Pd overlayer. This is an important finding and enables us to rationalize the observed steady-state cyclization activity of a novel type of colloidally derived, dispersed Au/Pd catalyst in which a core of Au is surrounded

by a thin shell of Pd: our model catalyst is a macroscopic analogue of these systems. Thus with the catalysts we find that the Pd-skinned particles, though active, are not as effective as those which result from deliberately alloying the core/shell particles by annealing procedures closely similar to those adopted here.

Why is the alloy more effective than pure Pd{111}? It seems likely that the two most important factors involve (i) degree of rehybridization of the adsorbed acetylene and (ii) strength of adsorption of the benzene product. With regard to (i), we know that the clean {111} surfaces of Pt, Rh, and Ir are ineffective in acetylene cyclization and that the molecule is much more strongly rehybridized than it is on Pd{111}: on these metals, under UHV conditions the only available reaction is decomposition to carbon and hydrogen. The weaker interaction with Pd-{111} preserves more alkyne bond character and cycloaddition reactions are possible. Consistent with this view, it is found that partial poisoning of Pt{111} by Sn renders the surface active for acetylene  $\rightarrow$  benzene conversion<sup>18</sup> and that clean Cu{110} is an even more efficient catalyst<sup>33</sup> than clean Pd{111} ( $\sim 80\%$ conversion in TPR versus  $\sim 25\%^{34}$ ). Thus it seems plausible that a reduced degree of interaction with the  $\sqrt{3}$  alloy surface should result in more efficient conversion of acetylene to benzene, the principal competing pathway being decomposition.<sup>1</sup> With regard to (ii), it is known that benzene desorbs from Pd-{111} with a (coverage dependent) degree of decomposition. Again, the weaker interaction and reduced binding with the alloy surface increase the probability of product desorption without decomposition.

### Conclusions

At 300 K Pd growth on Au{111} nucleates at the partial surface dislocations in the herringbone reconstruction, the overlayer islands appearing preferentially on the fcc domains of the substrate. XPS indicates little or no electronic perturbation of the Pd film.

The benzene yield in TPR measurements with acetylene may be rationalized in detail by reference to the STM images: deviation from an initial linear dependence coincides with the onset of second layer Pd growth before completion of the monolayer.

The catalytic efficacy of the Pd overlayer is a sensitive function of its morphology. Compared to smooth films, rough films display reduced activity and give rise to new binding sites for benzene.

Thermally induced Au/Pd surface alloy formation drastically alters the kinetics of benzene desorption and markedly increases the product yield. The alloy is a better catalyst than pure Pd.

The Au{111}/Pd model system provides useful insight into the performance and stability characteristics of supported Au/ Pd catalysts used for acetylene cyclization.

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