Langmuir
Article
pubs.acs.org/Langmuir

Structure−Reactivity Correlations in Pd−Au Bimetallic Nanoclusters[†]

Elad Gross and Micha Asscher*

Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received April 4, 2010. Revised Manuscript Received June 17, 2010

The effect of composition and morphology of bimetallic Pd−Au nanoclusters on their chemical reactivity has been studied with acetylene decomposition and conversion to ethylene and benzene as the chemical probe. High resolution transmission electron microscopy (HR-TEM) and CO-Temperature Programmed Desorption (TPD) measurements were employed for structure and chemical composition determination. Pd−Au clusters were prepared in ultrahigh vacuum (UHV) environment on SiO_2/Si(100) by direct deposition (DD) to form 2D bimetallic nanostructures. Different bimetallic cluster morphology could be obtained by employing the buffer layer assisted growth (BLAG) procedure with amorphous solid water as buffer material. The BLAG bimetallic clusters were found to be more reactive than DD particles toward acetylene hydrogenation to ethylene and trimerization to benzene. The morphology and composition of DD clusters enabled the formation of both tilted (low adsorption energy) and flat laying (high adsorption energy) benzene, while mainly tilted benzene was detected upon adsorption of acetylene on BLAG clusters. Moreover, the reactivity of bimetallic clusters was compared to that of thin Pd film. Strong preference (100:1 ratio) toward acetylene hydrogenation to ethylene over trimerization to benzene has been correlated with the lack of extended Pd(111) facets on the bimetallic clusters that suppress the benzene formation.

1. Introduction

Oxide supported metal clusters are widely used as model catalysts for industrial processes. It was demonstrated that a combination of two metals and the formation of bimetallic alloy clusters can modify their catalytic reactivity, dictated by the bimetallic clusters' geometry and electronic properties.[1−6] Nørskov et al. have shown that d-band electron energy has a dominant role in the clusters' catalytic reactivity. Therefore, by changing the energetic position of d-band electrons, for example, by bimetallic alloying, the overall reactivity can be modified.[4−6]

Enhancement of catalytic reactivity due to alloying has been demonstrated for acetylene trimetrization and hydrogenation over Pd−Au alloy extended surfaces and clusters. Reactivity of acetylene molecules following adsorption on various Pd surfaces has been studied in the last two decades. It was demonstrated that acetylene trimerization and hydrogenation are structure sensitive reactions with the Pd(111) facet as the most active surface.[7,8] Modifying the crystal structure from Pd(111) to Pd(110) and Pd(100) not only changed the catalytic yield but also modified the relative yield of the two competing reactions. While on Pd(111) the main product was benzene (3:1, benzene to ethylene ratio), on Pd(110) and Pd(100) the main product was ethylene (1:3 and 1:5, benzene to ethylene ratio, respectively). These results demonstrate that, on surfaces lacking hexagonal Pd sites or having high density of defects, hydrogenation is favored over trimerization.[9] Similar selectivity was obtained on pure Pd clusters (5 nm diameter) deposited on Al_2O_3 substrate. Upon adsorption of acetylene over these clusters, the measured ethylene to benzene ratio was 5:1.[10] This preference is correlated with the high density of surface Pd atoms having low coordination number.

Enhancement of benzene formation rates relative to clean Pd(111) were obtained over Pd−Au alloy substrates, prepared either by addition of gold atoms to extended Pd surfaces or by decoration of gold surfaces with Pd atoms.[11−14] A similar effect was reported due to addition of gold atoms to Pd clusters for a variety of other reactions, such as vinyl acetate (VA) synthesis[15] and the formation of olefins.[16] Introduction of defects to the oxide substrate enhanced the thermal stability and catalytic reactivity of the metal clusters, due to changes in the electronic properties of the substrate.[17−19]

Metallic nanoclusters supported on thin oxide films have been widely studied as model catalysts over the past two decades. The main preparation procedure of these catalysts has been via direct deposition (DD) of metal atoms on top of the oxide substrates,

---

[†] Part of the Molecular Surface Chemistry and Its Applications special issue.

*To whom correspondence should be addressed. E-mail: asscher@chem.ch.huji.ac.il.

(1) Chen, J. G.; Menning, C. A.; Zellner, M. B. *Surf. Sci. Rep.* **2008**, *63*, 201.
(2) Rodriguez, J. A. *Surf. Sci. Rep.* **1996**, *24*, 223.
(3) Studt, F.; Abild-Pedersen, F.; Bligaard, T.; Sorensen, R. Z.; Christensen, C. H.; Nørskov, J. K. *Science* **2008**, *320*, 1320.
(4) Nørskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. *Nat. Chem.* **2009**, *1*, 37.
(5) Hammer, B.; Nørskov, J. K. *Adv. Catal.* **2000**, *45*, 71.
(6) Kitchin, J. R.; Nørskov, J. K.; Barteau, M. A.; Chen, J. G. *Phys. Rev. Lett.* **2004**, *93*, 156801.
(7) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *Surf. Sci.* **1983**, *135*, 128.
(8) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *Chem. Commun.* **1983**, *11*, 625.
(9) Rucker, T. G.; Logan, M. A.; Gentle, T. .; Muetterties, E. L.; Somorjai, G. A. *J. Phys. Chem.* **1986**, *90*, 2703.
(10) Holmblad, P. M.; Rainer, D. R.; Goodman, D. W. *J. Phys. Chem. B.* **1997**, *101*, 8883.
(11) Baddeley, C. J.; Tikhov, M.; Hardacre, C.; Lomas, J. R.; Lambert, R. M. *J. Phys. Chem.* **1996**, *100*, 2189.
(12) Storm, J.; Lambert, R. M.; Memmel, N.; Onsgaard, J.; Taglauer, E. *Surf. Sci.* **1999**, *436*, 259.
(13) Ormerod, R. M.; Baddeley, C. J.; Lambert, R. M. *Surf. Sci. Lett.* **1991**, *259*, L709.
(14) Baddeley, C. J.; Barnes, C. J.; Wander, A.; Ormerod, R. M.; King, D. A.; Lambert, R. M. *Surf. Sci.* **1994**, *314*, 1.
(15) Chen, M. S.; Kumar, D.; Yi, C. W.; Goodman, D. W. *Science* **2005**, *310*, 291.
(16) Sarkany, A.; Geszti, O.; Safran, G. *Appl. Catal., A* **2008**, *350*, 157.
(17) Wallace, W. T.; Min, B. K.; Goodman, D. W. *J. Mol. Catal. A: Chem.* **2005**, *228*, 3.
(18) Parker, S. C.; Grant, A. W.; Bondzie, V. A.; Campbell, C. T. *Surf. Sci.* **1999**, *441*, 10.
(19) Landman, U.; Yoon, B.; Zhang, C.; Heiz, U.; Arenz, M. *Top. Catal.* **2007**, *44*, 145.

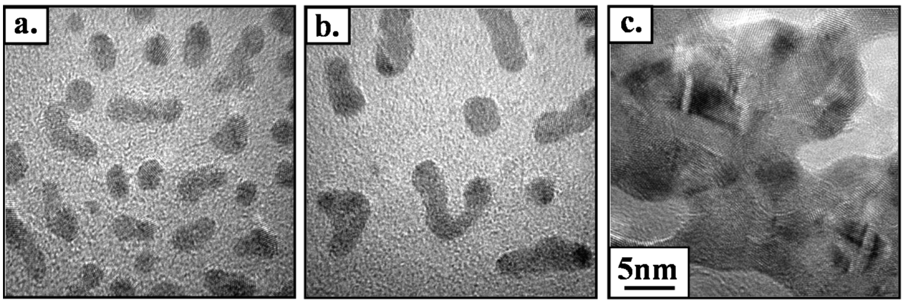

Figure 1. HR-TEM images of Pd−Au DD (a) and BLAG (b) clusters, prepared by simultaneous evaporation of 2 Å Pd and 2 Å Au and of a thick Pd film, prepared by direct evaporation of 20 Å Pd (c). All samples were prepared on a standard a-C TEM sample holder.

resulting in surface aggregation and the formation of metallic nanoclusters.[20,21] Introduction of weakly bound buffer layers to assist the growth of clusters has enabled better control over size and density of the deposited particles.[22] This cluster growth procedure, buffer layer assisted growth (BLAG), resulted in more 3D clusters when compared to DD clusters.[22−24] Recently, we have shown that by modifying the BLAG preparation procedure various compositions of Pd−Au clusters could be obtained.[25,26]

Here we report on a correlation found between the morphology and chemical composition of Pd−Au clusters on SiO_2/Si(100) as a model support, and their chemical reactivity. In order to better understand the unique reactivity and selectivity of the different bimetallic particles, the clusters' morphology and reactivity were compared to those of extended Pd films deposited on the same substrate. The role of cluster composition (Pd to Au ratio), size, and morphology on their reactivity and selectivity was determined. We conclude that a 1:1 Au to Pd ratio, verified by CO-Temperature Programmed Desorption (TPD) titration measurements, gives the most active bimetallic cluster. The Pd−Au alloy clusters promote ethylene formation over benzene by a unique preference factor of 100:1.

2. Experimental Section

Metal clusters were deposited on SiO_2/Si(100) substrate either by DD or by using amorphous solid water (ASW) as buffer material (BLAG), all within an ultrahigh vacuum (UHV) chamber equipped with standard surface cleaning and characterization capabilities, as previously described.[25] A native amorphous SiO_2 layer (~2.5 nm thick) on Si(100) was used as substrate. Prior to cluster preparation, the sample was annealed to 700 K, cleaned (mainly from carbon) by Ar^+ sputtering, and subsequently annealed once again to 700 K. The cleanliness of the oxide surface was verified by Auger electron spectroscopy measurements. SiO_2/Si(100) samples were attached to a stainless steel foil connected to a liquid nitrogen dewar via copper feedthroughs and two tantalum rods. A W26%Re-W5%Re thermocouple was spot-welded to the back side of the stainless steel foil. The actual silicon surface temperature was calibrated against multilayer water desorption at 165 K at a heating rate of 3 K/s. Au and Pd atoms were deposited using a resistively heated tungsten filament wrapped around Au or Pd (99.99% pure) wires, employing an in situ quartz microbalance (QMB) to determine deposition rates (1.2 ± 0.1 Å/min). Temperature programmed reaction (TPR) measurements were performed following adsorption of 3L ($1\ L = 10^{-6}$ Torr·s) C_2H_2 using a quadruple mass spectrometer (QMS) (RGA-200) in order to monitor the desorbing parent and product molecules. CO-TPD measurements were performed following exposure of the cold (120 K) sample to a saturation value of 30L CO. These measurements were performed in order to titrate the different binding sites and determine the total CO uptake by the various clusters. TPD and TPR spectra were all measured at a heating rate of 3 K/s.

Metallic clusters were grown also on top of a standard amorphous carbon (a-C) transmission electron microscopy (TEM) sample holder grid, attached in place of the silicon sample. In this case, the sample was annealed to 500 K prior to cluster preparation without sputter. The clusters' structure and elemental composition were determined using (ex situ, room temperature) high resolution (HR)-TEM measurements (Tecnai F20 G^2, nominal line resolution 0.1 nm).

Clusters prepared on a-C substrates were specifically studied and compared to silica supported clusters, addressing the potential substrates influence on cluster morphology. It was concluded that these surfaces did not significantly modify BLAG and DD nanocluster shape and stability. We therefore assume that the reactivity measured on silica is well represented by the bimetallic cluster morphology obtained by HR-TEM on a-C substrates.[26,27]

3. Results and Discussion

3.1. Chemical Reactivity versus Surface Composition.

3.1.1. HR-TEM and CO-TPD Characterization. Pd−Au clusters were prepared by two different methods. DD Pd−Au clusters were grown by simultaneous evaporation of 2 Å Au and 2 Å Pd on a cold (120 K) SiO_2/Si(100) substrate. In the second procedure, BLAG Pd−Au clusters were prepared by simultaneous evaporation of 2 Å Au and 2 Å Pd on top of an ASW buffer layer, 20 ML thick, followed by slow annealing of the sample to 165 K in order to remove the ASW layer and deposit the clusters. In order to calibrate the reactivity of Pd−Au alloy clusters, it was compared to that of a pure Pd substrate. Pd film was grown by direct evaporation of 20 Å Pd on top of the cold (120 K) silica substrate. HR-TEM images of DD and BLAG Pd−Au bimetallic clusters and of the pure Pd film are shown in Figure 1a, b and c, respectively, using standard amorphous carbon film on a copper grid as a substrate. BLAG clusters are more ramified and branched and at lower density compared to the DD clusters.[24,25] The fraction of the silica surface that is covered by metal particles is 8% and 15% for BLAG and DD clusters, respectively, while the thin Pd film covers 80% of the silica substrate.

CO-TPD and acetylene TPR measurements were conducted in order to investigate the surface elemental composition and overall reactivity of the different clusters. In these measurements, the clusters were prepared on SiO_2/Si(100) substrate as a model support. The actual surface elemental composition of the different samples was characterized by CO-TPD titration measurements.

---

(20) Baumer, M.; Freund, H. J. *Prog. Surf. Sci.* **1999**, *61*, 127.
(21) Lai, X.; St. Clair, T. P.; Valden, M.; Goodman, D. W. *Prog. Surf. Sci.* **1998**, *59*, 25.
(22) Huang, L.; Chey, S. J.; Weaver, J. H. *Phys. Rev. Lett.* **1998**, *80*, 4095.
(23) Waggoner, P. S.; Palmer, J. S.; Antonov, V. N.; Weaver, J. H. *Surf. Sci.* **2005**, *596*, 12.
(24) Gross, E.; Horowitz, Y.; Asscher, M. *Langmuir* **2005**, *21*, 8892.
(25) Gross, E.; Asscher, M. *Phys. Chem. Chem. Phys.* **2009**, *4*, 710.
(26) Gross, E.; Asscher, M. *J. Phys. Chem. C* **2009**, *113*, 18341.
(27) Schmidt, A. A.; Eggers, H.; Herwig, K.; Anton, R. *Surf. Sci.* **1996**, *349*, 301.

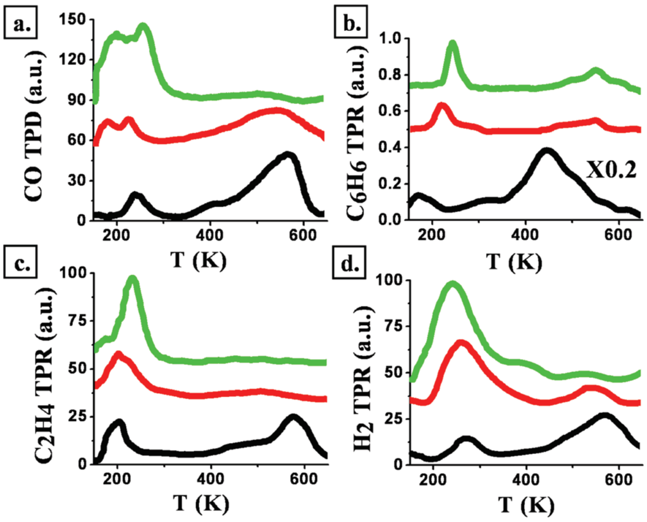

Figure 2. CO-TPD from BLAG (green), DD (red) bimetallic Pd–Au clusters, and from a Pd film (black) following exposure of 30L CO on the different substrates at 120 K (a). TPR results of benzene, ethylene, and hydrogen following exposure of 3L acetylene on the different substrates are shown in (b), (c), and (d), respectively.

CO-TPD from the Pd film contains two peaks, a minor low temperature one at 250 K and a major peak at 550 K (Figure 2a, black line). This spectrum is similar to that of a Pd(111) single crystal, in which two peaks at 200 and 450 K were reported having a similar intensity ratio.[28] Based on this comparison, the high temperature peak can be assigned to CO adsorbed on Pd threefold hollow sites, while the low temperature peak is attributed to CO adsorbed on Pd atop sites. Based on these TPD spectra, one may conclude that the surface structure of the Pd film on silica contains predominantly hexagonal threefold sites similar to an ordered Pd(111) surface. The TEM image in Figure 1c indeed reveals crystalline domains having the (111) character.

In contrast to the 20 Å thick Pd film, three peaks were observed in the CO-TPD spectra from DD Pd–Au clusters (Figure 2a, red line). The low temperature peak (180 K) is assigned to CO adsorbed on predominantly Au atoms, while the peak at 230 K is attributed to CO desorbing from Pd atop sites. CO desorption from Pd threefold sites corresponds to the high temperature peak (550 K). Similar intensity of the two low temperature peaks obtained from DD Pd–Au clusters suggests a 1:1 proportion between single Au and Pd atoms exposed on the surface of these bimetallic clusters. In addition, the difference in the high temperature part of the TPD spectra suggests a significant decrease in the density of Pd threefold hollow sites on DD clusters.

CO-TPD spectra from BLAG Pd–Au clusters revealed only two low temperature desorption peaks, attributed to desorption from Au and Pd atop sites, at a ratio of 1:1 (Figure 2a, green line). The absence of any high temperature CO desorption (threefold sites) indicates that there are practically no ensembles of three nearest-neighbor Pd atoms on the surface of BLAG Pd–Au clusters.[26] Similar suppression of the high temperature peak was obtained when Au atoms were directly evaporated over an extended Pd(111) single crystal surface. These measurements have shown that, upon annealing to 600 K, the Pd–Au alloy structure was formed on the surface, followed by a decrease in the CO high temperature desorption peak amplitude.[11] The bimetallic BLAG nanoclusters therefore seem to contain similar surface atomic composition, however, following a much lower preparation temperature (~200 K).

3.1.2. Chemical Reactivity. Acetylene reacts over Pd–Au clusters via two competing pathways: (a) decomposition that leads to ethylene and hydrogen and (b) trimerization to form benzene. All three products subsequently desorb via TPR, following adsorption of 3L of acetylene at 120 K.

In all three samples, the formation of ethylene and hydrogen has been the dominant reactivity channel. For all three product molecules, highest reactivity per Pd atom was that of the BLAG bimetallic clusters (marked by the green lines in Figure 2b–d).[26] The presence of a high temperature benzene TPR peak (~550 K) indicates that both DD and BLAG alloy clusters stabilize strongly bound benzene molecules. However, significant enhancement of the formation of tilted benzene has been detected on BLAG clusters as demonstrated by the increase in the low temperature (~250 K) desorption peak (Figure 2b, green line). These two effects are attributed to the 3D nature of BLAG Pd–Au clusters and to the formation of bimetallic alloy, as revealed by X-ray diffraction (XRD) measurements.[26] It should be noted that, on both DD and BLAG bimetallic clusters, ethylene and hydrogen formation was favored by 2 orders of magnitude over benzene.

There is a direct correlation between the ethylene and hydrogen TPR profiles in all three samples. This observation indicates that desorption of hydrogen and ethylene occurs at approximately the same temperature range. Ethylene and hydrogen TPR spectra from the thin Pd film have two dominant peaks (black curves in Figure 2c and d, respectively). The high temperature ethylene desorption peak (570 K) can be attributed to interaction of subsurface hydrogen with stable adsorbed fragments of acetylene molecules.[29] The formation of ethylene from acetylene at this temperature range was also obtained over pure Pd clusters prepared on Al_2O_3 substrate.[10]

The integrated areas under the ethylene and hydrogen TPR profiles obtained from the three different samples vary by only 30%. In contrast, reactivity toward benzene formation of the pure Pd film sample was higher than that of the other samples by more than 1 order of magnitude.

There are also differences in the relative yield of formation (selectivity) of the three products over the different samples. Two competing reaction pathways are considered: acetylene decomposition that leads to hydrogen and ethylene evolution or trimerization of acetylene to form benzene. The hydrogen formation is coupled to surface carbon accumulation that directly could not be quantified in this study. The highest decomposition to trimerization ratio was measured over BLAG clusters. Lower overall reactivity, of the DD sample, has preserved the proportion between the main two reactivity channels. In contrast, on the pure Pd thin film, the reactivity has changed to favor benzene formation, presumably due to a significant acceleration of benzene formation rate and its stabilization at high surface temperature.

Benzene formation is rather sensitive to the various samples as evident by the differences in the TPR profiles. While on the bimetallic clusters, both DD and BLAG, the dominant peak is always the low temperature peak (250 K), assigned to the formation of tilted benzene, the Pd film preferentially leads to the formation of the high temperature peak at 550 K, indicating the formation of flat laying benzene.

In order to provide a more quantitative "carbon balance" and to estimate the role of acetylene decomposition, we compared the TPD signal intensity obtained from the parent acetylene molecules following adsorption on the native SiO_2, on which acetylene does not react and on BLAG Pd–Au clusters. The acetylene TPD

---

(28) Guo, X.; Yates, J. T. *J. Chem. Phys.* **1989**, *90*, 6761.

(29) Shaikhutdinov, Sh.; Heemeier, M.; Baumer, M.; Lear, T.; Lennon, D.; Oldmen, R. J.; Jackson, S. D.; Freund, H. J. *J. Catal.* **2001**, *200*, 330.

signal intensity decreased by more than 40% upon adsorption on the bimetallic clusters. Based on TPR measurement, it can be concluded that less than half of the decomposed acetylene molecules have led to ethylene, hydrogen, and benzene formation. Considering the similar TPD signal of hydrogen and ethylene, it can be estimated that about 20% of the adsorbed acetylene molecules were totally decomposed to elemental carbon. A similar fraction hydrogenated to ethylene, while only less than 0.5% of the acetylene molecules converted to benzene.

The trimerization of acetylene to benzene was demonstrated to be a structure sensitive reaction, with Pd(111) being the most reactive facet. TPR measurements of a variety of Pd single crystals have shown that by changing the single crystal substrate from Pd(111) to Pd(110) and Pd(100) the ratio between ethylene to benzene formation rates is modified, to favor ethylene.[9] The fraction of acetylene molecules dissociating all the way to surface carbon has not been considered quantitatively in these studies.

On Pd−Au clusters that contain high density of defects and limited domains that contain extended Pd(111) facets, the formation of benzene becomes highly unfavorable. The competing reaction of hydrogenation to ethylene becomes faster and more probable by 2 orders of magnitude. In contrast, over Pd film, the formation of flat laying benzene is facilitated due to the 2D structure that consists of extended Pd(111) facets (Figure 1c).

Dominant low temperature (250−300 K) benzene TPR spectra were reported also for other bimetallic substrates such as Pd(111)/Au,[11] Au(111)/Pd,[13] and Pd + Au/Ru(001).[12] Suppression of the high temperature benzene TPR peak was attributed to the break-up of Pd ensembles and formation of Pd−Au alloy. In all these studies,[11−13] the preference toward ethylene formation has been less pronounced than that in this report. Finally, the accumulation of surface carbon poisons the catalytic reactivity of the bimetallic clusters, as evident by the significant overall reactivity reduction down to 10% of the initial run.

3.2. Acetylene Hydrogenation Mechanism. Hydrogenation of acetylene originates from decomposition of a fraction of the parent acetylene molecules, followed by reaction between the adsorbed hydrogen atoms with neighbor acetylene molecules leading to the formation of ethylene. Metallic cluster formation via the BLAG mechanism involves interaction between hot Pd atoms and water molecules within the ASW buffer layer. This may lead to water dissociation and to formation of reactive Pd−H species. Ethylene may then be formed from Pd−H upon reaction with neighbor acetylene molecules. In this case, the necessary hydrogen originates from water molecules and not from parent acetylene. In order to asses the role of the buffer layer in the acetylene hydrogenation process, H_2O ASW was substituted by D_2O as the buffer molecules. The TPR results of ethylene formation, following acetylene adsorption on BLAG Pd−Au clusters (prepared by simultaneous evaporation of 2 Å Au and 2 Å Pd) employing 20 ML D_2O as buffer layer, are shown in Figure 3.

More than 85% of the product ethylene molecules did not contain any deuterium atom (black curve), while 10% contained one (red curve) and less than 5% contained two deuterium atoms (green curve). Considering the 2% ^{13}C content in each of the ethylene molecules, one can estimate the contribution of the buffer D_2O molecules to the acetylene hydrogenation by the BLAG clusters to less than 8%. We conclude, therefore, that the hydrogenation reaction proceeds primarily as a result of partial decomposition of acetylene molecules upon adsorption on the BLAG Pd−Au bimetallic alloy clusters. The unique preparation method of the BLAG clusters, enabling the formation of bimetallic clusters, enhanced the overall reactivity and the preference for the formation of ethylene.

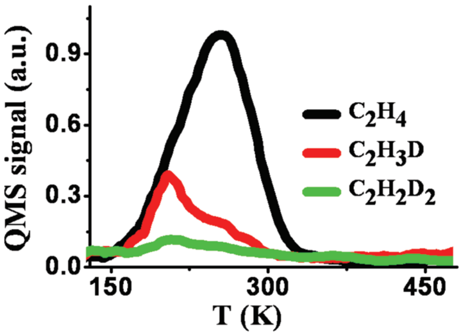

Figure 3. TPR of ethylene following adsorption of acetylene over BLAG Pd−Au clusters, prepared by simultaneous evaporation of 2 Å Au and 2 Å Pd on 20 ML of D_2O as buffer layer. TPR spectra of C_2H_4 (black), C_2H_3D (red), and $C_2H_2D_2$ (green) (masses 28, 29, and 30, respectively) are shown.

3.3. Effect of Pd/Au Elemental Ratio. In order to better understand the effect that Au atoms have on the reactivity of bimetallic Pd−Au clusters, we have varied the Pd/Au ratio during cluster preparation. The surface composition and reactivity of the bimetallic clusters were investigated by CO-TPD and acetylene TPR measurements.

CO-TPD spectra obtained from BLAG clusters containing different elemental proportion are shown in Figure 4a. Upon increasing the Au/Pd ratio, the high temperature CO desorption peak (550 K) has disappeared. This observation is well correlated with a decrease in the number of threefold hollow Pd sites. The gradual increase in the Au/Pd ratio results in the emergence of a low temperature peak (170 K), attributed to CO desorption from Au atoms,[30] while relatively minor changes were detected in CO desorption from Pd atop sites (250 K).

Reactivity toward benzene formation for different Au/Pd ratios is presented in Figure 4b. Changes in the elemental ratio had only a minor effect on the formation and stabilization of tilted benzene (low temperature benzene desorption peak at ~250 K). At a Au/Pd ratio of 1:1, flat laying benzene (high temperature benzene TPR peak at ~500 K) reached a maximum value. At this ratio, 3D bimetallic clusters were formed with their surface composed of Au and Pd atoms at a ratio of 1:1 (as titrated by CO TPD). Both tilted (250 K) and flat laying (500 K) benzene molecules were formed at this elemental ratio. The formation of flat laying benzene at this ratio is explained by stabilization of the benzene molecules due to the presence of a specific density of Au surface atoms, effectively preventing the decomposition of these flat laying benzene molecules upon annealing.[11]

CO-TPD titration of the DD clusters having different elemental composition is shown in Figure 4c. Increasing the Au/Pd ratio has led to an enhancement of CO desorption from Au atoms (180 K). At the same time, the desorption rate from Pd atop sites (230 K) only slightly decreased and the small contribution from the high temperature sites (550 K), assigned to desorption from Pd threefold sites, was unchanged.

The elemental content only marginally affects the reactivity of DD clusters with respect to the benzene TPR yield (Figure 4d). The formation of flat laying benzene on DD clusters may be explained by the 2D nature of DD clusters and the presence of more extended ensembles of Pd atoms with their threefold sites that stabilize the flat laying benzene molecules, even when the Pd content has decreased.

---

(30) Gross, E.; Lundwall, M.; Goodman, D. W.; Asscher, M. *J. Phys. Chem. C* **2007**, *111*, 16199.

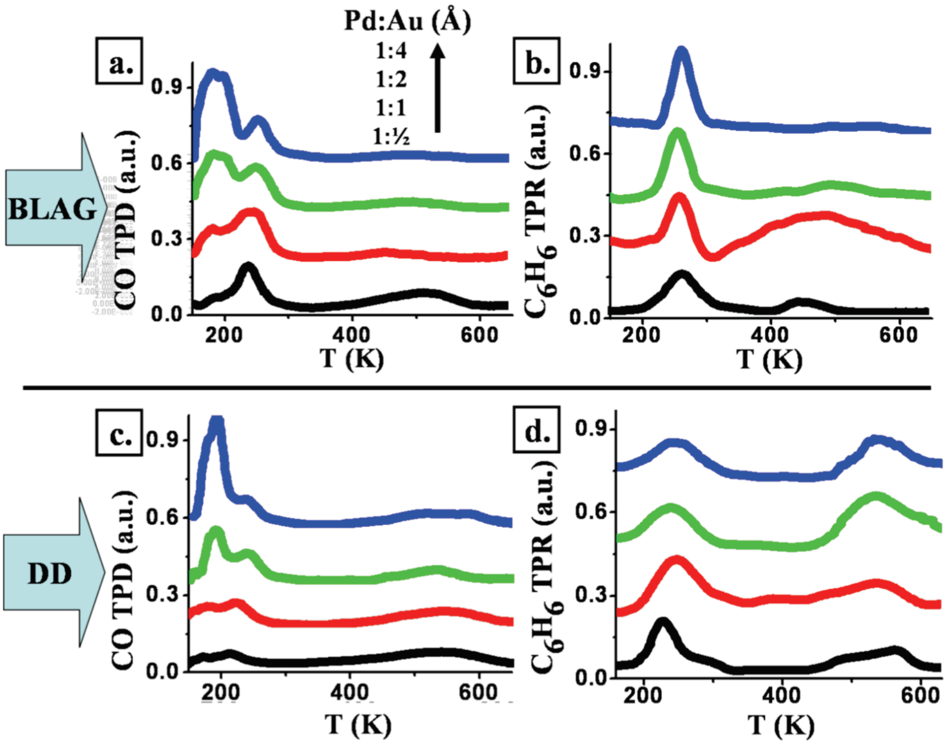

Figure 4. CO-TPD (a,c) and TPR (b,d) of benzene from BLAG (a,b) and DD (c,d) recorded following exposure to 30L CO and 3L C_2H_2 (respectively) while changing the proportion between the Pd and Au elements. Pd and Au dosage are indicated in the figure.

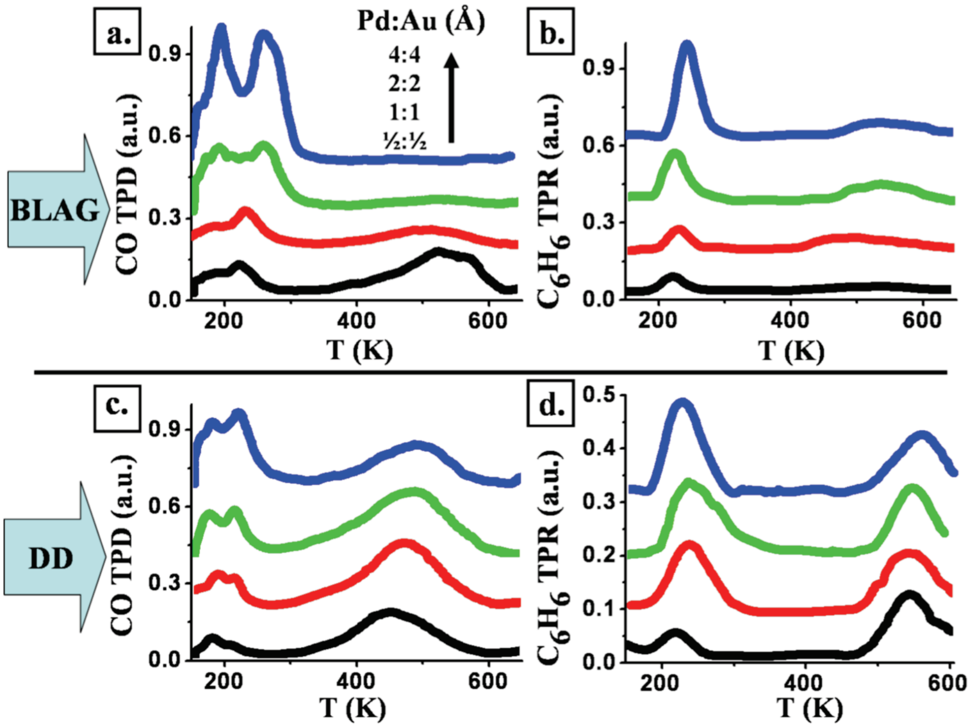

Figure 5. CO-TPD (a,c) and TPR (b,d) of benzene from BLAG (a,b) and DD (c,d) observed following exposure to 30L CO and 3L C_2H_2 (respectively) while changing the overall dosage at a fixed Pd/Au ratio. Pd and Au dosage are indicated in the figure.

3.4. Overall Metal Dosage. Increasing the total amounts of evaporated Au and Pd influences the size and morphology of bimetallic clusters and their chemical reactivity.

A monotonic increase in the uptake from the two low temperature CO TPD peaks was observed for both BLAG and DD clusters (Figure 5a and c, respectively). Unlike the BLAG clusters, however, CO-TPD from DD clusters contains a fraction of desorbing molecules from Pd threefold sites. It turns out that the fraction of the relevant Pd ensembles is rather insensitive to the total metal dosage. Increasing the amount of evaporated metal significantly enhanced the total CO uptake from BLAG clusters, while only a smaller increase was monitored from DD clusters. These observations are presumably associated with differences in the cluster morphology. 3D BLAG clusters are known to be strongly modified by any increase in the metal dosage, unlike the more 2D nature of DD clusters.[23,25,26]

The presence of fixed ensembles of Pd atoms on the 2D domains of the DD clusters enhanced the formation and stabilization of flat laying benzene molecules which desorbed at relatively high temperature (550 K) (Figure 5d). Increasing the total dose led to an increase in the formation of tilted benzene (230 K) in the case of DD clusters. This can be correlated with the observed increase in CO uptake from Pd atop and Au sites, indicating the formation of Pd−Au alloy having a fixed elemental composition. The effect of the overall increase of metal dosage results in selective enhancement of the tilted benzene formation, in the case of BLAG clusters (Figure 5b), which can be rationalized by the 3D nature of these particles and the formation of Pd−Au alloy.

4. Conclusions

Elemental and structural analysis of bimetallic Au−Pd clusters has been correlated with their chemical reactivity. These measurements have demonstrated that the bimetallic BLAG particles are more active than DD clusters toward both acetylene self-hydrogenation to ethylene and trimerization to benzene. HR-TEM images and CO-TPD titration have correlated between the 3D morphology of the BLAG clusters and their bimetallic alloy composition. DD clusters, in contrast, are more 2D in nature, thus stabilizing threefold Pd domains. These differences in the composition and morphology of DD and BLAG clusters were maintained even when the total metal dosage increased by an order of magnitude or when the Pd/Au composition ratio was modified.

Upon adsorption of acetylene on BLAG clusters, mainly tilted benzene molecules were formed and stabilized, while on DD clusters both tilted and flat laying benzene molecules were observed. The 2D morphology seems to support extended ensembles of Pd atoms that in turn stabilize both flat laying and tilted benzene molecules.

The reactivity of bimetallic clusters (DD and BLAG) was calibrated against a thin Pd film. We found that on bimetallic clusters the complete decomposition channel (20% yield) and ethylene formation (20% yield) were favored by 2 orders of magnitude over trimerization reaction to form benzene. On the pure Pd film, decomposition and hydrogenation of acetylene were only 1 order of magnitude more probable than trimerization. The stronger preference of bimetallic clusters to hydrogenate and decompose acetylene has been correlated with the relatively low density of threefold Pd ensembles on these clusters.

To conclude, structure−reactivity correlations of the kind described in this work are predicted to provide deep insight into the specific and unique reactivity and selectivity of bimetallic clusters as heterogeneous catalysts in general, not limited to the Pd−Au case.

Acknowledgment. Partial support by ACS-PRF Grant, the US-Israel Binational Science Foundation and the Israel Science Foundation is acknowledged. E.G. is grateful for a generous fellowship given by The Eshkol Foundation, administered by Israel Ministry of Science.