# Acetylene Reactivity on Pd–Cu Nanoparticles Supported on Thin Silica Films: The Role of the Underlying Substrate

E. Sorek,<sup>†</sup> J. Ankri,<sup>†</sup> G. Arbiv,<sup>†</sup> R. Mol,<sup>†</sup> I. Popov,<sup>‡</sup> H.-J. Freund,<sup>§</sup> S. Shaikhutdinov,<sup>§</sup> and M. Asscher\*,<sup>†</sup>

<sup>†</sup>Institute of Chemistry, Edmond J. Safra Campus, The Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel <sup>‡</sup>The Harvey M. Krueger Family Center for Nanoscience and Nanotechnology, The Hebrew University, Jerusalem 91904, Israel <sup>§</sup>Department of Chemical Physics, Fritz-Haber Institute der Max-Planck Gesellschaft, Faradayweg 4-6, Berlin D-14195, Germany

Supporting Information

ABSTRACT: Heterogeneous chemistry that develops on ultrathin films such as bilayer  $SiO_2/Ru(0001)$  is interesting as a model catalysis system. We have studied the partial decomposition and hydrogenation of acetylene to ethylene and its trimerization to benzene on Pd-Cu bimetallic alloy nanoparticles (NPs) supported on those thin silica films. In comparing the bilayer  $SiO_2/Ru(0001)$  to thicker silica layers without a metallic substrate, for example, the native  $SiO_2/Si(100)$ , the size distribution of the clusters is narrower on the bilayer  $SiO_2/Ru(0001)$  substrate, demonstrating the effect of the underlying metal in preventing cluster diffusion during their growth. In addition, the effect of medium pressure on the NP shape has been investigated via transmission electron microscopy imaging of the NPs on relatively



thick SiO<sub>2</sub>. The NPs become elongated when exposed to 0.2 mbar acetylene inside a moderate-pressure cell embedded within an ultrahigh vacuum (UHV) chamber. By changing the elemental composition of the NPs on both substrates, the important effect of the suboxide material on catalyst reaction selectivity has been demonstrated. However, the effect of the composition of the bare NPs is not enough to actually define the long-term activity of a catalyst. In order to address more realistic conditions, we performed consecutive reactivity cycles by adsorbing acetylene at 110 K with subsequent annealing up to 400 K in UHV on the same  $1Pd:1Cu NPs/bilayer SiO_2/Ru(0001)$  catalyst. This revealed a strong decrease in the selectivity toward ethylene, from an ethylene/benzene product yield ratio of  $370 \pm 150$  in the first cycle down to  $50 \pm 15$  during the third to fifth cycles. Carbon atom accumulation on the metallic particles in the first and subsequent runs is the main reason for this modification in selectivity. A consecutive reactivity study uniquely demonstrates how rapidly and significantly the catalyst's performance is modified during the initial stages of its heterogeneous catalytic reactivity.

# 1. INTRODUCTION

The properties of supported metal catalysts are largely determined by metal-support interactions.<sup>1,2</sup> In order to model these interactions with control at the atomic level using surface science tools, thin oxide films are grown on singlecrystal metal supports.<sup>3-10</sup> These layers may be of sufficient thickness to model bulk support or they may be thin, for example, a few layers in thickness, to allow the species supported on the oxide to interact with the underlying oxide supporting metal. It has been demonstrated that such an experimental<sup>11</sup> approach, in conjunction with theory,<sup>12,13</sup> allows for conceptual studies on how charge transfer affects the morphology and chemistry of supported metal nanoparticles (NPs).<sup>14-16</sup>

Typically, metal NPs are created by physical vapor deposition of a metal or consecutively by deposition of several metals onto a bare oxide film at a suitable temperature.<sup>4,5,17</sup> However, better control of the created metal (or bimetallic) NPs may be achieved by using buffer layer-assisted deposition.<sup>18–20</sup>

For the model catalyst in our study, we utilized the alloy's effects on reactivity and selectivity.  $^{21,22}$  To this end, bimetallic particles were deposited on top of a well-ordered bilayer of the  $SiO_2$  film grown on top of a Ru(0001) surface. The structure of the silica film has been studied extensively in recent years.<sup>23-25</sup> It is noteworthy that the SiO<sub>2</sub> bilayer appears as a crystalline or a vitreous film. It is therefore of interest to compare its properties as a metal NP support with an equivalent amorphous layer of silica grown as the native oxide on a silicon substrate.

In this report, we describe the mechanism underlying the reactivity of acetylene for the formation of ethylene and benzene because of supported bimetallic Pd-Cu NPs on the thin silica on ruthenium substrate. This reactivity is then compared to studies under identical conditions (the same Pd-Cu bimetallic clusters) on top of the relatively thick (about 2.5 nm) amorphous native silica grown on the Si(100)

**Received:** May 18, 2019 Revised: June 20, 2019 Published: June 25, 2019

substrate.<sup>26</sup> Where the oxide layer is very thin, charge transfer may occur between the suboxide metal and the metallic NPs on top. For gold deposited on thin MgO/Ag(001), the clusters' shape is affected by electron transfer from the silver–oxide interface below the oxide film through the thin MgO film to the gold nanoclusters, in order to satisfy the electronegative nature of the gold.<sup>13,27</sup> This is in contrast to thick MgO films, where gold atoms remained neutral.

In our study, because copper's electronegativity is lower than that of Ru (and Pd is similar to Ru), the electrons may be transferred in the opposite way, from copper-palladium clusters to ruthenium through the thin silica layer. It was recently shown that Pd and even Au donate electrons to Ru through a silica bilayer.<sup>28</sup> Silica films were also found to increase the work function of the metal, therefore lowering the probability of electron transfer from the metal to the clusters.<sup>25</sup> As a result, the clusters on the thin silica preserve their hemispherical shape in order to minimize the positive Coulomb repulsion. As for the influence of this charge on the catalytic performance of the metallic NPs, we can assume that this effect is relatively minor. The contribution of positive versus negative charging on catalytic reactivity has been studied by density functional theory calculations. It was concluded that positive charging has a very limited effect on catalytic reactivity.<sup>30</sup>

The initial step in acetylene hydrogenation toward ethylene formation lies in its decomposition.<sup>31</sup> Next, reactions between adsorbed hydrogen atoms with neighboring but not yet decomposed acetylene molecules leads to their hydrogenation to ethylene formation.<sup>19</sup> On the other hand, to create the conditions under which acetylene could be trimerized, the parent molecule should remain intact.<sup>32</sup> Controlling this first dehydrogenation rate will determine the ethylene/benzene selectivity.

In order to correlate between the model's ultrahigh vacuum (UHV) single adsorption-reaction-desorption cycle and the industrial high-pressure multiple reactivity cycles at each site, one can repeat the UHV single process several times. During dehydrogenation of acetylene, the active sites are expected to be partially poisoned by carbon atoms or alkenes;<sup>33</sup> thus, the next reactants will no longer meet the same catalytic sites as did the first ones.

# 2. EXPERIMENTAL SECTION

The experiments were performed in a UHV chamber where the bilayer crystalline  $SiO_2$  was grown on top of a Ru(0001) single-crystal metallic substrate. A silicon atom deposition device (Dual e-beam evaporator, Tectra) was employed with oxygen at a base pressure of  $10^{-7}$  Torr and a ruthenium crystal at 110 K. The surface was oxidized at 1200 K with oxygen at a base pressure of  $10^{-6}$  Torr before and after silicon deposition, following standard sputter–annealing cleaning cycles of the Ru(0001) substrate. This procedure was previously described in detail.<sup>24</sup>

Subsequently, metallic NPs, both pure atoms and bimetallic clusters, were deposited on top of the bilayer  $SiO_2/Ru(0001)$  substrate described above, using the water buffer layer-assisted growth (BLAG) method previously discussed.<sup>18–20</sup> Two independent evaporation instruments were employed: the Tectra dual e-beam deposition instrument for Si deposition and a separate double beam thermal evaporator with 0.25 mm diameter tungsten wire wrapped around 1 mm diameter Pd or Cu wires (Alfa Aesar, 99.95% purity) for clean metal NP

deposition via the BLAG method. In addition, a temperatureprogrammed desorption (TPD) setup (using an SRS-200 quadrupole mass spectrometer) and mini-Auger spectrometer (LK Technologies) were used for both indirect morphology determination of the bilayer SiO<sub>2</sub> film and for monitoring the substrate following the reactivity tests in UHV. A mediumpressure cell was introduced at the bottom of this chamber, enabling the reactions to be performed at pressures up to 10 Torr. The interior of this chamber was electroplated by a few micron-thick film of gold in order to minimize the contribution to the catalytic reaction from the walls. Following in situ quartz microbalance monitoring and preparation of the Pd-Cu bimetallic particles within the UHV chamber, and after being characterized by Auger spectroscopy and CO-TPD, the sample can be inserted into the medium-pressure cell at an acetylene pressure of 0.2 mbar. In order to better characterize the metal NPs, the bilayer  $SiO_2/Ru(0001)$  sample was removed from the UHV chamber and was ex situ inspected by high-resolution scanning electron microscopy (SEM) to evaluate the uniformity level of the silica film and the bimetallic NPs on top (used to indicate the quality and continuity of the silica substrate). In addition, the ruthenium substrate was replaced by a transmission electron microscopy (TEM) sample holder with  $SiO_2$  film (30–40 nm thick) on a copper grid, on top of which the metallic NPs were grown via the BLAG method. In this way, we could evaluate the crystallization level of these nanoclusters in addition to their spatial and size distributions.

#### 3. RESULTS AND DISCUSSION

**3.1. Bilayer SiO<sub>2</sub>/Ru(0001) Surface.** Various structure determination methods were employed in the past in order to identify the nature and morphology of the thin silica film grown on Ru(0001).<sup>23,24</sup> Here, we used a simple morphology determination tool based on Xe TPD. This method cannot distinguish between the crystalline or the amorphous phases of silica film; nevertheless, it provides a way to assess the imperfections within the SiO<sub>2</sub> layer. Figure 1 shows the TPD spectra of Xe desorbing from clean Ru(0001) and from the bilayer SiO<sub>2</sub>/Ru(0001) samples, following adsorption at 30 K.

The TPD spectra in Figure 1 are characterized by two desorption peaks at 93-100 K and 65 K. The high-temperature peak reflects the Xe ML desorption from clean Ru(0001), whereas the low-temperature peak is that of the multilayer. At the ML peak, we can see that the interaction of



Figure 1. Xe–TPD from clean Ru(0001) (black), oxygen-covered Ru(0001) (red), and bilayer  $SiO_2/Ru(0001)$  (blue) surfaces. Two monolayers (MLs) of Xe were exposed at a surface temperature of 30 K; the heating rate was 2 K/s.

Xe with the substrate is different on the clean versus the oxygen- and silica-covered ruthenium surfaces. Stronger Xe-Xe repulsive interaction is evident by the wide TPD peak (black) observed on clean ruthenium, centered at 95 K. In contrast, desorption of xenon from the oxygen-covered ruthenium (red) is a significantly narrower peak centered at 100 K, which is also characteristic of pure first-order desorption kinetics. The Xe interaction with the adsorbed oxygen atoms appears to be slightly stronger than that with the clean ruthenium atoms. Moreover, the Xe-O interaction apparently eliminates the repulsive interaction among the adsorbed Xe atoms. The Xe-SiO<sub>2</sub> interaction is similar to the one with the adsorbed oxygen (a desorption peak is also at 100 K); however, the relevant TPD spectrum suggests a lower sticking probability of Xe on  $SiO_2/Ru(0001)$  or, more likely, a smaller number of adsorption sites, as evident from the lower intensity of the desorption peak. It also suggests that this hightemperature peak reflects and titrates the open ruthenium sites that were not fully covered by the silica film. The lowtemperature peak near 65 K remains at almost the same intensity for all three samples, and it reflects the second layer of Xe, which is expected to be less sensitive to the substrate.

In addition to TPD, we removed the sample from the vacuum chamber and examined its SEM images after depositing the Pd-Cu clusters as markers, as shown in Figure 2. One can clearly see the dark area that is due to a fraction of



**Figure 2.** SEM image of the bilayer  $SiO_2/Ru(0001)$  sample following Pd–Cu nanocluster growth via BLAG. One can see the bare (dark area) O-covered Ru(0001) that is maintained during the standard growth sample procedure, leaving about 5–10% uncovered Ru(0001) substrate. The dots throughout the remaining image are Pd–Cu nanoclusters grown via the BLAG procedure on the silica layer at 110 K. At higher magnification, one can see the metallic alloy NPs also deposited on the bare oxidized ruthenium.

the ruthenium substrate that was not covered by the  $SiO_2$  layer. It turns out that about 5–10% of the ruthenium was not covered by the silica (a number extracted from larger image areas), consistent with previous studies.<sup>24</sup> CO-TPD measurements (not shown) were performed to ensure the high  $SiO_2$  coverage. This is in reasonable agreement with the Xe–TPD shown in Figure 1.

**3.2. Bimetallic Pd–Cu Alloy Clusters.** As discussed in the Experimental Section, the bimetallic clusters were grown/ deposited on the bilayer  $SiO_2/Ru(0001)$  substrate by the BLAG procedure. The buffer material was amorphous solid water (ASW), and the metal atoms were simultaneously deposited on top of 20 MLs of ASW at 110 K. Pd–Cu bimetallic nanoclusters were subsequently softly deposited on the  $SiO_2/Ru(0001)$  substrate upon desorption of the buffer

ASW film at 165 K, resulting in clusters' typical size range of 5  $\pm$  2 nm. We attempted to investigate the role of the underlying Ru(0001) metallic substrate on the chemistry (acetylene decomposition with subsequent hydrogenation to ethylene and its trimerization to benzene) developed on top of the bimetallic clusters and compared it to similar reactivity studies performed earlier on the SiO<sub>2</sub>/Si(100) substrate.<sup>26</sup>

The morphology of these clusters has been analyzed by employing TEM and SEM imaging following exposure to moderate acetylene pressure (0.2 mbar), as displayed in Figure 3. A more detailed structural analysis is provided in Supporting



Figure 3. Images of Pd–Cu NPs on different  $SiO_2$  substrates, deposited in UHV via BLAG with subsequent exposure to acetylene: (A) TEM image of Pd–Cu NPs grown on  $SiO_2/Cu$  mesh (TEM) substrate and then exposed to 0.2 mbar@450 K for 40 min within the embedded medium-pressure cell. (B) SEM image of the Pd–Cu NPs grown on the thin bilayer  $SiO_2/Ru(0001)$  substrate and then exposed to 0.2 mbar@600 K for 40 min. (C) Pd–Cu bimetallic NP size (area) distribution of the NPs shown in (A) (black bars) and (B) (red bars).

Information Figure S1. The high exposure to acetylene is possible by employing an embedded moderate pressure cell (up to 10 Torr) within our UHV chamber. It is clearly shown in Figure 3 that upon exposure of the bimetallic Pd-Cu NPs prepared on the  $SiO_2/Si(100)$  substrate to 0.2 mbar acetylene, significant sintering or aggregation takes place when the sample is heated up to 450 K for 40 min (Figure 3A). In contrast, when the same NPs were prepared on the bilayer SiO<sub>2</sub>/ Ru(0001) substrate, the clusters' size distribution remained almost unchanged at around  $5 \pm 2$  nm in diameter (Figure 3B) even following exposure to 0.2 mbar acetylene at a higher temperature (600 K). This demonstrates the stability and sintering resistance nature of the clusters caused by the underlying ruthenium, presumably resulting from charge transfer through the thin silica bilayer, as mentioned above. The particles' size (area of the particles in nm<sup>2</sup>) distribution on top of the two  $SiO_2$  layers is shown in Figure 3C.

Although the enhanced stability of the NPs induced by Ru below the  $SiO_2$  bilayer preserves their morphology under significant exposure and high annealing temperature conditions, making them sintering resistant, the clusters'

aggregation on the SiO<sub>2</sub>/Si(100) substrate (lacking the underlying metal stabilizer) in the presence of 0.2 mbar acetylene starts already at room temperature (demonstrated in Supporting Information Figure S2A–C). Apparently, the main effect of the elevated pressure, namely, a high rate of acetylene molecule collisions, is the clusters' surface mobility on the SiO<sub>2</sub>/Si(100) substrate, which leads to their sticking to each other and becoming larger and elongated.

High-resolution (aberration-corrected) TEM imaging of single bimetallic clusters, prepared within the UHV environment, have demonstrated the expected crystal morphology of the Pd–Cu alloy (1:1 ratio) obtained from the diffraction pattern analysis of the structure in Figure 4A. (The diffraction



Figure 4. (A) TEM image of a single bimetallic Pd–Cu alloy nanocluster deposited on a  $SiO_2/Cu$  mesh TEM sample holder. (B) EDS results of a line scan, shown in C over a single aggregated bimetallic cluster. (C) Line scan across a single particle with a colored elemental distribution.

pattern is shown in Supporting Information Figure S1). In addition, the elemental (C, Cu, Pd) distribution across a single, elongated, aggregated bimetallic nanocluster is shown in Figure 4B,C utilizing the EDS analysis. The presence of carbon on the bimetallic clusters was observed following the exposure of the sample to acetylene. The 1:1 ratio between Pd and Cu observed by the energy-dispersive spectrometry (EDS) analysis (Figure 4B) along the line scan of a single particle (Figure 4C) supports the data obtained in situ within the UHV chamber by the quartz microbalance instrument.

**3.3.** Acetylene Reactivity Over the Bilayer SiO<sub>2</sub>/Ru(0001) Surface. 3.3.1. Role of the NP Elemental Composition. Following the structural analysis of the samples described above, we performed reactivity tests with these samples as model catalysts. Figure 5A,B shows how changing the elemental composition ratio between Cu and Pd in the alloy nanoclusters affects the formation of the resulting ethylene and benzene products (Cu was kept fixed at 3 Å, whereas Pd was varied from 1 to 5 Å, both are of nominal thickness measured by an in situ quartz microbalance). Ethane, which is another potential product of acetylene decomposition, was not found at the minimum sample temperature at which



**Figure 5.** TPR spectra of the two products (ethylene and benzene) obtained following an acetylene  $({}^{13}C_2H_2)$  catalytic reaction, at varying alloy nanocluster elemental compositions. (A) Benzene  $({}^{13}C_6H_6, 84 \text{ amu})$  and (B) ethylene  $({}^{13}C_2H_4, 30 \text{ amu})$  formation rates detected (via TPR) at the indicated alloy elemental composition ratios (in Angstrom units). (C) Integrated area under the TPR peaks shown in A and B as the Pd–Cu ratio increases from pure copper (left) to pure palladium (right).

we ran the reaction (110 K), as expected where the ensembles of pure Pd sites are very small.<sup>34</sup>

Although for benzene formation (always the minor product) the most reactive composition was 1Pd:3Cu (the black-filled squares in Figure 5C), the highest ethylene formation rate was found with the elemental composition of 5Pd/3Cu (the blue-filled squares in Figure 5C).

The results of the nanoclusters' elemental composition effect on the acetylene decomposition and the related selectivity between the two main products (ethylene and benzene) reveals a gradual increase in both the overall decomposition rate of acetylene and the selectivity toward ethylene formation as the fraction of Pd increases from 1:3 to 5:3 (Pd:Cu). This may be understood because the ethylene product formation rate increases when the fraction of palladium increases, whereas that of benzene decreases. We can conclude that the growing presence of Pd atoms at the surface of the alloy NPs is the most important feature for increasing the selectivity of the acetylene decomposition reaction toward ethylene formation.

The selectivity changes resulting from the elemental composition changes within Pd–Cu NPs can be summarized based on the temperature-programmed reaction (TPR) data in Figure 5 by considering Figure 5C, which demonstrates the integrated TPR signals of these products. This is presented in Figure 6 as a bar graph. Here, we compare the results obtained from the bilayer SiO<sub>2</sub> on the ruthenium substrate (black bars) to the results of the same acetylene decomposition reaction reported on top of similar Pd–Cu NPs, however, when deposited on top of the amorphous native silica on the bulk Si(100) substrate (red bars).<sup>26</sup> With amorphous, native silica on Si(100), the selectivity does not change appreciably, with an ethylene-to-benzene formation ratio of  $8 \pm 5$  when the elemental ratio changes from 1:3 to 5:3 (Pd:Cu).

A possible explanation for the effect of the substrate is the partial negative charge transfer from the bimetallic clusters to the ruthenium metallic substrate via the bilayer  $SiO_2$  because



**Figure 6.** Products' selectivity (ethylene-to-benzene ratio) resulting from acetylene decomposition on the Pd–Cu nanoclusters, as a function of the elemental composition in the clusters: Cu is fixed at 3 Å and the Pd varies from 1 to 5 Å. The black bars represent the results obtained from the bilayer SiO<sub>2</sub> on Ru(0001) and the red bars represent the results obtained from the native SiO<sub>2</sub> (2.5 nm) on Si(100). Note the order of magnitude difference between the two Y axis scales.

of differences in the electronegativity mentioned in the introduction. The stabilization of the clusters on the bilayer silica caused by the repulsive forces, because of the positive charge of the clusters, enhances their reactivity toward ethylene. Without stabilization, the effect of increasing Pd dosage is less significant owing to some (even if small at low temperatures) aggregation of the clusters.

One can observe that reduced Pd atom content and surface coverage in an NP affect not only the selectivity but also the desorption temperature of the products, as shown in Figure 5A. The high-temperature desorption peak shifts down from 450–500 to 370 K as the Pd content decreases. Thus, the adsorption of a benzene becomes weaker because each molecule is attached to a fewer Pd atoms.

Comparing the reactivity of the Pd–Cu alloy clusters to that of the pure palladium or copper clusters (see Figure 5) on SiO<sub>2</sub>/Ru(0001) shows that palladium produced practically no benzene at all and that the benzene yield of the copper is relatively low. As expected, regarding ethylene production, we see the opposite trend, where palladium is more efficient than copper. However, it is clearly shown that for both products the alloy is significantly more efficient than the pure metals and that the efficiency and selectivity are controllable. This synergetic contribution of the alloy is valid also on the SiO<sub>2</sub>/ Si(100) substrate (not shown), but in that case, the Pd is more efficient than Cu for both ethylene and benzene production.

3.3.2. Multiple Reaction Cycles. It is well understood that the elemental composition of prepared NPs in UHV does not serve as a particularly realistic model of the catalyst operating under industrial conditions because of the possible effect of deposited residues of the parent molecules. Here, the expected additional atom in addition to the metallic NPs is carbon (or CH groups) because of the decomposition of acetylene. In addition, in moderate- to high-pressure catalytic reactions, where the turnover number is more than unity, it is rather difficult or impossible to identify the initial changes (structural and surface elemental composition). The NPs undergo changes that may affect the reactivity and selectivity of the catalyst. In contrast, under a model UHV environment, one may run a single reactivity cycle at a time, namely, adsorbing the reactant and letting it react while a single TPR run is monitored by means of the mass spectrometry of the desorbing products (and nonreacting parent molecules). Numerous

cycles can be repeated on top of the just reacted catalyst without cleaning or otherwise modifying it. In this way, one can follow the changes that the reactivity and selectivity undergo every single cycle.

These kinds of measurements were performed on the 3Pd:3Cu and 1Pd:3Cu NPs (see Figure 7). The actual TPR results are shown in the Supporting Information, Figures S3A–D and S4A,B.



**Figure 7.** Selectivity toward ethylene formation expressed by the ratio of the area under the TPR peaks at mass 30  $({}^{13}C_2H_4)$  to that at mass 84  $({}^{13}C_6H_6)$  as observed in four consecutive cycles of acetylene decomposition. The reaction took place over layers of 3Pd:3Cu (black) and 1Pd:3Cu (red) NPs on top of a bilayer SiO<sub>2</sub>/Ru(0001) catalyst under UHV.

When we repeated the reaction on top of the same catalyst (in UHV) for consecutive runs, a significant change was observed in the relative formation rates of the two products (ethylene/benzene), obtained from the integral over the entire TPR spectra of the two relevant masses, as shown in Figure 7. The drop in the selectivity toward ethylene was most significant after the first run (see the black bars in Figure 7). The value for the selectivity of  $370 \pm 150$  obtained for the 3Pd:3Cu sample represents the average of five independent measurements.

As shown in Figure 3, on the bilayer  $SiO_2/Ru(0001)$ , the morphology of the Pd-Cu NPs does not change significantly even upon heating up to 600 K. We therefore can conclude that the main reason for the impressive drop in selectivity toward ethylene, as seen in Figure 7, is due to the gradual increase in the carbon surface coverage (or CH groups) on the NPs after each consecutive reaction. In situ Auger spectra taken before and following the TPR runs at gradually higher exposures to acetylene reveal an increasing carbon signal following exposure to acetylene and the subsequent reaction. The Auger spectra are shown in Supporting Information Figure S5. The carbon atoms observed on the NPs by ex situ EDS measurements following a single run of acetylene decomposition (Figure 4B,C) qualitatively suggest the role of the carbon atom accumulation on the surface in modifying the catalyst's selectivity. Moreover, the carbon EDS signal seems to follow the profile of the palladium signal (blue curve) more precisely than that of the copper one (green curve).

These results are supported by a previous study showing that carbon adsorbed on Pd particles inhibits dehydrogenation reaction pathways of other molecules.<sup>35</sup> In our case, this dehydrogenation is the initial step that will finally lead to ethylene formation (by leaving free hydrogen atoms on the surface, which are available for acetylene hydrogenation). Dehydrogenation inhibition increases the presence of the

parent molecules, which are intact on the surface, enabling their trimerization to benzene. The desorption profile of the ethylene product also changes with the number of consecutive reaction cycles. Although in the first run the high-temperature desorption peak is centered near 300 K (see Supporting Information Figure S3), as the number of cycles increases, the high-temperature peak diminishes and a low-temperature double peak near 130-180 K grows and becomes the dominant one after the fourth/fifth cycle. This demonstrates how by changing the surface composition the thermal binding energy of the product to the surface may be strongly affected. Unlike the ethylene product, the benzene desorption peak remains at about the same desorption temperature (230 K) (reflecting the same binding energy to the surface). However, it increases in its intensity, as the product yield increases. Apparently, partial blocking of the Pd atoms' adsorption sites for the acetylene molecules (by carbon) improves the reaction yield toward benzene formation (and at the same time decreases the reaction rate toward ethylene formation).

Because 1Pd:3Cu alloy particles have revealed the lowest ethylene/benzene selectivity within a single reactivity cycle, we also performed a series of consecutive reactions over a Pddeficient bimetallic sample [1Pd:3Cu/bilayer SiO<sub>2</sub>/Ru(0001)] (see the red bars in Figure 7). The support for the important role played by the surface Pd atoms is demonstrated in Supporting Information Figure S4 via the TPR spectra. As the palladium surface concentration decreases, the ethylene formation yield drops with it and the selectivity toward ethylene decreases as well. Starting from a ethylene/benzene ratio of  $370 \pm 150$  in the first cycle on clean 3Pd:3Cu clusters, on 1Pd:3Cu clusters from the 4th cycle, it reaches the point where the selectivity no longer exists (the ethylene/benzene ratio is just slightly above 1). The effective Pd surface density decreases because of the initial bimetallic Pd-Cu nanoclusters' preparation (from 3Pd:3Cu down to the 1Pd:3Cu clusters) or by the apparent preferential deposition of carbon atoms on top of the surface Pd atoms. Both cases lead to reduced rates of ethylene formation. It is worth mentioning that in spite of the carbon accumulation on the NP surface as a result of the reaction, the morphology of the clusters and their perfect bimetallic alloy structure were not affected, as postreactivity SEM imaging revealed (not shown).

#### 4. CONCLUSIONS

We studied the reactivity of acetylene over bimetallic Pd-Cu nanoclusters deposited via the BLAG procedure under an UHV environment on top of two different silica substrates. The substrates were the native oxide  $(SiO_2)$  (2.5 nm thick)/ Si(100) and a 2D crystalline silica bilayer (0.6 nm thick) grown on the Ru(0001) substrate. Two main questions were addressed: (1) does the substrate influence the clusters' size distribution, and (2) does it affect the chemical reactivity? Although, as prepared, the bimetallic clusters' size distribution is not significantly affected, the reactivity and in particular, the selectivity of our model reaction is. The bimetallic clusters on the bilayer  $SiO_2/Ru(0001)$  substrate reveal a higher and more controllable selectivity than the same clusters on thick silica. This is apparently due to their stability/sintering resistance during the reaction. Because the metallic NPs do not remain clean under realistic reaction conditions, we have performed multiple reactivity cycles on the same set of metallic NPs as a model for the changing catalyst during reactions. Importantly, we found that the reactivity of acetylene to ethylene and

benzene changes in its selectivity toward ethylene formation, according to the number of reactivity cycles in UHV. It dropped from the ethylene/benzene formation ratio of  $370 \pm 150$  (the first cycle) down to about  $50 \pm 15$  from the third cycle on the 3Pd:3Cu clusters. Over the 1Pd:3Cu samples deposited on the bilayer SiO<sub>2</sub>/Ru(0001), the selectivity was significantly lower. The TEM analysis revealed that the carbon atom residues, which are spread on top of the bimetallic clusters, are the most probable reason for this significant drop in selectivity. This unique observation can be made only under model UHV conditions, revealing how rapidly the nature of a catalyst's reactivity and selectivity changes while operating under typical industrial, high-pressure conditions. This may also explain the typical "conditioning" industrial catalysts undergo in order to operate in a stable manner.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b04722.

Additional TEM analysis of the NPs, including size distribution and surface analysis using Auger spectroscopy and detailed TPRs of the multicycle reactions (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: micha.asscher@mail.huji.ac.il.

#### ORCID 0

H.-J. Freund: 0000-0001-5188-852X S. Shaikhutdinov: 0000-0001-9612-9949

M. Asscher: 0000-0002-4476-5617

# Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This study was partially supported by the German-Israeli Foundation (GIF grant number 1236). We would like to acknowledge the help of Marcelo Friedman and Dr. Edvard Mastov for their technical support.

#### REFERENCES

(1) Ertl, G.; Knözinger, H.; Schüth, F.; Weitkamp, J. Handbook of *Heterogeneous Catalysis*, 8 Volume Set; Wiley, 2008.

(2) Farmer, J. A.; Campbell, C. T. Ceria Maintains Smaller Metal Catalyst Particles by Strong Metal-Support Bonding. *Science* 2010, 329, 933–936.

(3) Jian-Wei, H.; Estrada, C. A.; Corneille, J. S.; Ming-Cheng, W.; Wayne Goodman, D. CO Adsorption on Ultrathin MgO Films Grown on a Mo(100) Surface: An IRAS Study. *Surf. Sci.* **1992**, *261*, 164–170.

(4) Holmblad, P. M.; Rainer, D. R.; Goodman, D. W. Particle Size Effects in the Acetylene Cyclotrimerization on Planar Model Al2O3 Thin Film Supported Pd Clusters. *J. Phys. Chem. B* **1997**, *101*, 8883–8886.

(5) Campbell, C. T. Ultrathin Metal Films and Particles on Oxide Surfaces: Structural, Electronic and Chemisorptive Properties. *Surf. Sci. Rep.* **1997**, *27*, 1–111.

(6) Freund, H.-J. Adsorption of Gases on Complex Solid Surfaces. Angew. Chem., Int. Ed. Engl. 1997, 36, 452–475.

(7) Freund, H.-J.; Goodman, D. W. Ultrathin Oxide Films. Handbook of Heterogeneous Catalysis; American Cancer Society, 2008; pp 1309–1338. https://doi.org/10.1002/9783527610044.het-cat0071.

(8) Harding, C.; Habibpour, V.; Kunz, S.; Farnbacher, A. N.-S.; Heiz, U.; Yoon, B.; Landman, U. Control and Manipulation of Gold Nanocatalysis: Effects of Metal Oxide Support Thickness and Composition. J. Am. Chem. Soc. **2009**, 131, 538–548.

(9) Shaikhutdinov, S.; Freund, H.-J. Ultrathin Silica Films on Metals: The Long and Winding Road to Understanding the Atomic Structure. *Adv. Mater.* **2013**, *25*, 49–67.

(10) Freund, H.-J. The Surface Science of Catalysis and More, Using Ultrathin Oxide Films as Templates: A Perspective. *J. Am. Chem. Soc.* **2016**, *138*, 8985–8996.

(11) Cui, Y.; Stiehler, C.; Nilius, N.; Freund, H.-J. Probing the Electronic Properties and Charge State of Gold Nanoparticles on Ultrathin MgO versus Thick Doped CaO Films. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92* (). https://doi.org/10.1103/Phys-RevB.92.075444. DOI: 10.1103/physrevb.92.075444

(12) Frondelius, P.; Häkkinen, H.; Honkala, K. Adsorption of Small Au Clusters on MgO and MgO/Mo: The Role of Oxygen Vacancies and the Mo-Support. *New J. Phys.* **2007**, *9*, 339.

(13) Pacchioni, G.; Giordano, L.; Baistrocchi, M. Charging of Metal Atoms on Ultrathin MgO/Mo (100) Films. *Phys. Rev. Lett.* **2005**, 94 (). https://doi.org/10.1103/PhysRevLett.94.226104. DOI: 10.1103/ physrevlett.94.226104

(14) Freund, H.-J. Metal-Supported Ultrathin Oxide Film Systems as Designable Catalysts and Catalyst Supports. *Surf. Sci.* 2007, 601, 1438–1442.

(15) Sauer, J.; Freund, H.-J. Models in Catalysis. Catal. Lett. 2015, 145, 109–125.

(16) Pacchioni, G.; Freund, H.-J. Controlling the Charge State of Supported Nanoparticles in Catalysis: Lessons from Model Systems. *Chem. Soc. Rev.* **2018**, *47*, 8474–8502.

(17) Heemeier, M.; Carlsson, A. F.; Naschitzki, M.; Schmal, M.; Bäumer, M.; Freund, H.-J. Preparation and Characterization of a Model Bimetallic Catalyst: Co–Pd Nanoparticles Supported on Al2O3. Angew. Chem., Int. Ed. **2002**, *41*, 4073–4076.

(18) Huang, L.; Chey, S. J.; Weaver, J. H. Buffer-Layer-Assisted Growth of Nanocrystals: Ag-Xe-Si(111). *Phys. Rev. Lett.* **1998**, *80*, 4095–4098.

(19) Gross, E.; Asscher, M. Structure–Reactivity Correlations in Pd–Au Bimetallic Nanoclusters. *Langmuir* **2010**, *26*, 16226–16231.

(20) Gross, E.; Asscher, M.; Lundwall, M.; Goodman, D. W. Gold Nanoclusters Deposited on SiO2 via Water as Buffer Layer: CO-IRAS and TPD Characterization. *J. Phys. Chem. C* 2007, 111, 16197–16201.

(21) Edwards, J. K.; Solsona, B.; Landon, P.; Carley, A. F.; Herzing, A.; Watanabe, M.; Kiely, C. J.; Hutchings, G. J. Direct Synthesis of Hydrogen Peroxide from H2 and O2 Using Au–Pd/Fe2O3 Catalysts. *J. Mater. Chem.* **2005**, *15*, 4595–4600.

(22) Gao, F.; Goodman, D. W. Pd-Au Bimetallic Catalysts: Understanding Alloy Effects from Planar Models and (Supported) Nanoparticles. *Chem. Soc. Rev.* 2012, *41*, 8009–8020.

(23) Freund, H.-J. Controlling Silica in Its Crystalline and Amorphous States: A Problem in Surface Science. *Acc. Chem. Res.* 2017, 50, 446–449.

(24) Lichtenstein, L.; Heyde, M.; Freund, H.-J. Crystalline-Vitreous Interface in Two Dimensional Silica. *Phys. Rev. Lett.* **2012**, *109*, 106101.

(25) Löffler, D.; Uhlrich, J. J.; Baron, M.; Yang, B.; Yu, X.; Lichtenstein, L.; Heinke, L.; Büchner, C.; Heyde, M.; Shaikhutdinov, S.; et al. Growth and Structure of Crystalline Silica Sheet on Ru(0001). *Phys. Rev. Lett.* **2010**, *105*, 146104.

(26) Murugadoss, A.; Sorek, E.; Asscher, M. Structure and Composition of Au-Cu and Pd-Cu Bimetallic Catalysts Affecting Acetylene Reactivity. *Top. Catal.* **2014**, *57*, 1007–1014.

(27) Yulikov, M.; Sterrer, M.; Heyde, M.; Rust, H.-P.; Risse, T.; Freund, H.-J.; Pacchioni, G.; Scagnelli, A. Binding of Single Gold Atoms on Thin MgO(001) Films. *Phys. Rev. Lett.* **2006**, *96*, 146804.

(28) Büchner, C.; Lichtenstein, L.; Stuckenholz, S.; Heyde, M.; Ringleb, F.; Sterrer, M.; Kaden, W. E.; Giordano, L.; Pacchioni, G.; Freund, H.-J. Adsorption of Au and Pd on Ruthenium-Supported Bilayer Silica. J. Phys. Chem. C 2014, 118, 20959–20969.

(29) Giordano, L.; Cinquini, F.; Pacchioni, G. Tuning the Surface Metal Work Function by Deposition of Ultrathin Oxide Films: Density Functional Calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2006, 73, 045414.

(30) Molina, L.; Hammer, B. The Activity of the Tetrahedral Au20 Cluster: Charging and Impurity Effects. J. Catal. 2005, 233, 399–404. (31) Al-Ammar, A. S.; Webb, G. Hydrogenation of Acetylene over Supported Metal Catalysts. Part 2.—[ 14 C]Tracer Study of Deactivation Phenomena. J. Chem. Soc., Faraday Trans. 1 1978, 74,

657–664. (32) Patterson, C. H.; Lambert, R. M. Molecular Mechanisms in the Cyclotrimerization of Acetylene to Benzene on Palladium (111). *J. Phys. Chem.* **1988**, *92*, 1266–1270.

(33) Sárkány, A.; Schay, Z.; Stefler, G.; Borkó, L.; Hightower, J. W.; Guczi, L. Hydrogenation of 1,3-Butadiene over Catalysts Prepared from Amorphous Pd2Ni50Nb48 Ribbon: Effect of Self-Poisoning on Competitive Adsorption. *Appl. Catal. Gen.* **1995**, *124*, L181–L187.

(34) Zhang, Y.; Diao, W.; Williams, C. T.; Monnier, J. R. Selective Hydrogenation of Acetylene in Excess Ethylene Using Ag- and Au– Pd/SiO2 Bimetallic Catalysts Prepared by Electroless Deposition. *Appl. Catal. Gen.* **2014**, *469*, 419–426.

(35) Brandt, B.; Fischer, J.-H.; Ludwig, W.; Libuda, J.; Zaera, F.; Schauermann, S.; Freund, H.-J. Isomerization and Hydrogenation of Cis-2-Butene on Pd Model Catalyst. *J. Phys. Chem. C* **2008**, *112*, 11408–11420.