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

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

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Abstract

Heterogeneous chemistry that develops on ultra-thin films such as bilayer SiO₂/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 nano-particles (NPs) supported on those thin silica films. In comparing the bilayer SiO₂/Ru(0001) to thicker silica layers without metallic substrate, e.g., the native SiO₂/Si(001), the size distribution of the clusters is narrower on the bilayer SiO₂/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 NP shape has been investigated via transmission electron microscopy (TEM) imaging of the NPs on relatively thick SiO₂. The NPs become elongated when exposed to 0.2 mbar acetylene inside a moderate-pressure cell embedded within an ultra-high vacuum (UHV) chamber. By changing the elemental composition of the NPs on both substrates, the important effect of the sub-oxide 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 110K with subsequent annealing up to 400K in UHV on the same 1Pd:1Cu NPs/bilayer SiO₂/Ru(0001) catalyst. This revealed a strong decrease in the selectivity towards ethylene, from an ethylene/benzene product yield ratio of 370±150 in the first cycle down to 50±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. 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.\textsuperscript{1,2} In order to model these interactions with control at the atomic level using surface science tools, thin oxide films are grown on single-crystal metal supports.\textsuperscript{3–10} These layers may be of sufficient thickness to model bulk support or they may be thin, e.g., 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\textsuperscript{11} approach, in conjunction with theory,\textsuperscript{12,13} allows for conceptual studies on how charge transfer affects the morphology and chemistry of supported metal nano-particles.\textsuperscript{14–16}

Typically, metal nano-particles 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.\textsuperscript{4,5,17} However, better control of the created metal (or bimetallic) nano-particles may be achieved by using buffer-layer-assisted deposition.\textsuperscript{18–20}

For the model catalyst in our study, we utilized the alloy’s effects on reactivity and selectivity.\textsuperscript{21,22} To this end, bimetallic particles were deposited on top of a well-ordered bilayer of SiO\textsubscript{2} film grown on top of a Ru(0001) surface. The structure of the silica film has been studied extensively in recent years.\textsuperscript{23–25} It is noteworthy that the SiO\textsubscript{2} bilayer appears as a crystalline or a vitreous film. It is therefore of interest to compare its properties as a metal nano-particle 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 due to 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 Si(100) substrate. Where the oxide layer is very thin, charge transfer may occur between the sub-oxide metal and the metallic nano-particles on top. If gold deposition exists on thin MgO film on 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 nano-clusters, in order to satisfy the electronegative nature of the gold. This is in contrast to thick MgO films, where gold atoms remained neutral.

In our study, since 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. 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. 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 vs. negative charging on catalytic reactivity has been studied by DFT calculations. It was concluded that positive charging has a very limited effect on catalytic reactivity.

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

In order to correlate between the model’s 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, so 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 110K. The surface was oxidized at 1200K 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.$^{24}$

Subsequently, metallic nano-particles, 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.$^{18-20}$ Two independent evaporation instruments were employed: the Tectra dual e-beam deposition instrument for Si deposition and a separate double beam thermal evaporator with 0.25mm diameter tungsten wire wrapped around a 1 mm diameter Pd or Cu wires (Alfa Aesar, 99.95% purity) for clean metal NP deposition via the BLAG method. In addition, a temperature programmed desorption (TPD) set-up (using an SRS-200 quadrupole mass spectrometer) and a mini-Auger spectrometer (LK Technologies) were used for both indirect morphology determination of the bilayer SiO$_2$ film and for monitoring the substrate following the reactivity tests in UHV. A medium-pressure 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 microns-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 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 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 nano-clusters in addition to their spatial and size distributions.

3. Results and Discussion

3.1 Bilayer SiO\textsubscript{2}/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).\textsuperscript{23,24} Here we used a simple morphology determination tool based on Xe temperature programmed desorption (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\textsubscript{2} layer. Figure 1 shows the TPD spectra of Xe desorbing from clean Ru(0001) and from the bilayer SiO\textsubscript{2}/Ru(0001) samples, following adsorption at 30K.

![Figure 1: Xe-TPD from clean Ru(0001) (black), oxygen-covered Ru(0001) (red), and bilayer SiO\textsubscript{2}/Ru(0001) (blue) surfaces. Two monolayers (MLs) of Xe were exposed at a surface temperature of 30K; the heating rate was 2K/sec.]

The TPD spectra in Figure 1 are characterized by two desorption peaks at 93-100K and at 65K. The high temperature peak reflects the Xe monolayer desorption from clean Ru(0001), whereas the low temperature peak is that of the multilayer. At the monolayer peak we can see that the interaction of Xe with the substrate is different on the clean vs. the oxygen- and the silica-covered ruthenium surfaces. Stronger Xe-Xe
repulsive interaction is evident by the wide TPD peak (black) observed on clean ruthenium, centered at 95K. In contrast, desorption of xenon from the oxygen-covered ruthenium (red) is a significantly narrower peak centered at 100K, which is also characteristic of pure first-order desorption kinetics. The Xe interaction with the adsorbed oxygen atoms appears to be slightly stronger than with the clean ruthenium atoms. Moreover, the Xe-O interaction apparently eliminates the repulsive interaction among the adsorbed Xe atoms. The Xe-SiO$_2$ interaction is similar to the one with the adsorbed oxygen (a desorption peak is also at 100K); 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 high temperature peak reflects and titrates the open ruthenium sites that were not fully covered by the silica film. The low temperature peak near 65K 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 Scanning Electron Microscopy (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 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$^{24}$ 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.
Figure 2: SEM image of the bilayer SiO$_2$/Ru(0001) sample following Pd-Cu nano-cluster 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 nano-clusters grown via the BLAG procedure on the silica layer at 110K. At higher magnification one can see the metallic alloy NPs also deposited on the bare oxidized ruthenium.

3.2 The 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 buffer layer assisted growth (BLAG) procedure. The buffer material was amorphous solid water (ASW) and the metal atoms were simultaneously deposited on top of 20 monolayers of ASW at 110K. Pd-Cu bimetallic nano-clusters were subsequently softly deposited on the SiO$_2$/Ru(0001) substrate upon desorption of the buffer ASW film at 165K, resulting in clusters' typical size range of 5±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$_2$/Si(100) substrate.$^{26}$

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 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 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 450K for 40 minutes (Figure 3A). In contrast, when the same NPs were prepared on the bilayer SiO$_2$/Ru(0001) substrate, the clusters' size distribution remained almost unchanged at around 5±2 nm in diameter (Figure 3B) even following exposure to 0.2 mbar acetylene at a higher temperature (600K). 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$^2$) distribution on top of the two SiO$_2$ layers is shown in Figure 3C.
Whereas 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$_2$/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 S2 (A, B, 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$_2$/Si(100) substrate, which leads to their sticking to each other and becoming larger and elongated.

**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, then exposed to 0.2 mbar @450K for 40 minutes within the embedded medium-pressure cell. (B) SEM image of the Pd-Cu NPs grown on the thin bilayer
SiO$_2$/Ru(0001) substrate, then exposed to 0.2 mbar @600K for 40 minutes. (C) Pd-Cu bimetallic nano-particle size (area) distribution of the NPs shown in A (black bars) and B (red bars).

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. In addition, the elemental (C, Cu, Pd) distribution across a single, elongated, aggregated bimetallic nano-cluster is shown in Figures 4B and 4C utilizing 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 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 micro-balance instrument.
Figure 4: (A) TEM image of a single bimetallic Pd-Cu alloy nano-cluster 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.

3.3 Acetylene reactivity over the bilayer SiO$_2$/Ru(0001) surface

3.3.1 The 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 5 (A and B) shows how changing the elemental composition ratio between Cu and Pd in the alloy nano-clusters 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 micro-balance). Ethane, which is another potential product of acetylene decomposition, was not found at the minimum sample temperature at which we ran the reaction (110K), as expected where the ensembles of pure Pd sites are very small.$^{34}$

Whereas 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).
Figure 5: Temperature programmed reaction (TPR) spectra of the two products (ethylene and benzene) obtained following an acetylene \((^{13}\text{C}_2\text{H}_2)\) catalytic reaction, at varying alloy nano-cluster elemental compositions. (A) Benzene \((^{13}\text{C}_6\text{H}_6, 84 \text{ amu})\) and (B) ethylene \((^{13}\text{C}_2\text{H}_4, 30 \text{ amu})\) 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).

The results of the nano-clusters’ 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 towards ethylene formation as the fraction of Pd increases from 1:3 to 5:3 (Pd:Cu). This may be understood since 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 towards 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$_2$ 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). The variation observed when the bilayer silica substrate is on ruthenium is more significant and monotonous, revealing a growing selectivity towards ethylene as the fraction of Pd atoms increases with an order of magnitude increase from 1:3 to 5:3 (Pd:Cu). With amorphous, native silica on Si(100), the selectivity does not change appreciably, with an ethylene-to-benzene formation ratio of 8±5 when the elemental ratio changes from 1:3 (Pd:Cu) 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$_2$, due to differences in the electronegativity mentioned in the introduction. The stabilization of the clusters on the bilayer silica caused by the repulsive forces, due to 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 atoms content and surface coverage in a NP affects 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 450-500K to 370K as the Pd content decreases. Thus, the adsorption of a benzene becomes weaker since each molecule is attached to a fewer Pd atoms.
Figure 6: Products’ selectivity (ethylene to benzene ratio) resulting from acetylene decomposition on the Pd–Cu nano-clusters, as a function of the elemental composition in the clusters: Cu is fixed at 3Å and the Pd varies from 1 to 5Å. The black bars represent the results obtained from the bilayer SiO2 on Ru(0001) and the red bars represent the results obtained from the native SiO2 (2.5 nm) on Si(100). Note the order of magnitude difference between the two Y axis scales.

Comparing the reactivity of the Pd-Cu alloy clusters to that of the pure palladium or copper clusters (see Figure 5) on SiO2/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 SiO2/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 due to 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) due to 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 non-reacting 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 the reactivity and selectivity undergo every single cycle.

These kinds of measurements were performed on the 3Pd:3Cu and the 1Pd:3Cu NPs (see Figure 7). The actual TPR results are shown in Supporting Information, Figures S3 (A, B, C, D) and S4 (A, B).

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 towards ethylene was most significant after the first run (see the black bars in Figure 7). The value for the selectivity of 370±150 obtained for the 3Pd:3Cu sample represents the average of 5 independent measurements.
Figure 7: The selectivity towards ethylene formation expressed by the ratio of the area under the TPR peaks at mass 30 (13C2H4) to that at mass 84 (13C6H6) as observed in 4 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 SiO2/Ru(0001) catalyst under UHV.

As shown in Figure 3, on the bilayer SiO2/Ru(0001), the morphology of the Pd-Cu NPs does not change significantly even upon heating up to 600K. We therefore can conclude that the main reason for the impressive drop in selectivity towards 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 (Figures 4B and 4C) 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.35 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. Whereas in the first run the high temperature desorption peak centered near 300K (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 (230K) (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 towards benzene formation (and at the same time decreases the reaction rate towards ethylene formation).

Since 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 Pd-deficient bimetallic sample (1Pd:3Cu/bilayer SiO$_2$/Ru(0001)) (see the red bars in Figure 7). 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 towards ethylene decreases as well. Starting from an ethylene/benzene ratio of 370±150 in the first cycle on clean 3Pd:3Cu clusters, on 1Pd:3Cu clusters from the 4$^{th}$ 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 nano-clusters’ 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 post reactivity SEM imaging revealed (not shown).

4. Conclusions

We studied the reactivity of acetylene over bimetallic Pd-Cu nano-clusters 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 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 a more controllable selectivity than the same clusters on thick silica. This is apparently due to their stability/sintering resistance during the reaction. Since 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 towards ethylene formation, according to the number of reactivity cycles in UHV. It dropped from the ethylene/benzene formation ratio of 370±150 (the first cycle) down to about 50±15 from the third cycle on the 3Pd:3Cu clusters. Over the 1Pd:3Cu sample deposited on the bilayer SiO₂/Ru(0001), the selectivity was significantly lower. 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.

Supporting information

Additional TEM analysis of the NPs, including size distribution and surface analysis using Auger spectroscopy and detailed TPRs of the multi-cycle reactions, are provided.

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200:1
C₃H₂
1:1
Ru Pd Cu Si O
1:200 1:1