

Acetylene Cyclotrimerization on Supported Size-Selected Pd_n Clusters (1 ≤ n ≤ 30): One Atom Is Enough!

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Abstract: We studied the cyclotrimerization of acetylene on size-selected Pd_n clusters (1 ≤ n ≤ 30) supported on thin MgO(100) films by thermal desorption and Fourier transform infrared spectroscopy. Surprisingly, the production of benzene is already observed on a single palladium atom at low temperature (300 K). Using density functional theory (DFT) calculations we show that free inert Pd atoms are activated by charge transfer from defect sites of the MgO substrate upon deposition. For larger clusters (7 ≤ n ≤ 30) benzene is additionally produced at a temperature of 430 K and our results suggest the existence of a critical ensemble of seven palladium atoms for this high-temperature reaction mechanism.

1. Introduction

In a structure-sensitive reaction the catalytic properties vary with the size of the active particles, most often small clumps of metal atoms.¹ In general, the observed size effects can be classified into two ranges.² For particles hundreds or thousands of atoms in size, the size dependence is essentially related to atom packing and consequently the concomitant variation of step and kink densities^{3,4} on the particle surface is responsible for the observed size-dependent catalytic properties.^{5,6} It was shown that this changing morphology can sensitively influence the kinetics of a reaction.⁷ In the size range where metal clusters consist only of a few atoms, the size-dependent catalytic activity for free^{8–11} and supported^{12–15} clusters is directly related to their intrinsic electronic and geometric properties. For example, the catalytic oxidation of carbon monoxide on small size-selected

supported platinum and gold clusters shows atom-by-atom size dependence. In these studies the observed size effects can be rationalized by the distinct electronic and geometric structure of each cluster size and by assuming a size-dependent interaction of the small clusters with the substrate.^{16–19}

Motivated by the suggestion that purely geometric arguments can explain the observed structure sensitivity in the cyclotrimerization of acetylene to benzene on palladium single crystals^{20,21} and on supported palladium particles,²² we performed a study of this reaction on small, size-selected supported palladium clusters. On single crystals the reaction proceeds readily at pressures ranging from UHV (10⁻¹²–10⁻⁸ atm) to atmospheric pressure (10⁻¹–1 atm) and Pd(111) is found to be the most reactive facet.^{23,24} These studies established the following overall reaction pathway: In the first step C₂H₂ is adsorbed in 3-fold sites and at low temperature (<200 K) a stable surface intermediate C₄H₄ is formed that results from the combination of two adsorbed acetylene molecules.²⁵ Addition of a third activated acetylene molecule leads then to the formation of benzene (~200 K). At high coverage or pronounced surface roughness, the formed benzene is forced into a weaker binding configuration with the molecular axis tilted

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with respect to the surface. From this tilted configuration benzene desorbs already at a temperature of 230 K. At low coverage and on flat surfaces the formed C₆H₆ binds strongly to the surface in a flat-lying configuration desorbing at a temperature of ~500 K.^{26,27} It is believed that the reaction takes place without C–C bond scission,²⁸ and it appears that in the first step acetylene is adsorbed in the 3-fold hollow site on palladium^{25,29} via two σ -bonds and a π -bond (di- σ/π configuration). This configuration leads to adsorbed C₂H₂ in a flat-lying geometry and the electronic structure is grossly distorted from sp¹ to sp^{2.5} hybridization^{30,31} resulting in slightly bent acetylene molecules. However, these studies also show that the existence of isolated 3-fold sites alone is not a sufficient condition for the cyclotrimerization of acetylene, but it is suggested that the catalytically effective surface ensemble corresponds to three C₂H₂ molecules adsorbed on 3-fold sites around a given Pd atom.^{25,29} This geometrical requirement is perfectly fulfilled for an ensemble of seven Pd atoms of the Pd(111) surface,^{26,32} and it is this argument that explains the structure sensitivity of the cyclotrimerization reaction. The formation of benzene on palladium particles a few nanometers in size is very similar to the analogous low-index single-crystal results, with desorption of benzene at 230 and 530 K.²² The larger palladium particles in this series, regular polyhedra comprised exclusively of $\langle 111 \rangle$ and $\langle 100 \rangle$ facets, favor the low-temperature reaction pathway whereas the smaller particles desorb benzene at 530 K. In addition, all investigated particles reveal production of benzene at 370 K, which is related to defect sites. The results on small size-selected Pd_{*n*} (1 ≤ *n* ≤ 30) clusters on thin MgO(100) films presented here show pronounced size effects in the cyclization of three acetylene molecules. Most surprisingly, already a single palladium atom adsorbed on MgO is enough for the production of benzene at 300 K. Although a free Pd atom is inert for this reaction, once adsorbed on the surface the charge transfer from defect sites of the basic MgO substrate activates the metal atom. On larger clusters (Pd_{*n*}, *n* > 8) benzene is mainly produced at a temperature of around 430 K. Our results show that this 430 K feature is first observed for deposited Pd₇, the critical ensemble for this high-temperature mechanism.

2. Experimental and Computational Details

The palladium clusters are produced by a recently developed high-frequency laser evaporation source.³³ The positively charged cluster ions are guided by home-built ion optics through differentially pumped vacuum chambers and are size-selected by a quadrupole mass spectrometer (Extranuclear C50/mass limit: 4000 amu). The monodispersed clusters are deposited with low kinetic energy (0.1–2 eV) onto a magnesium oxide surface. The total energy of the deposition is composed of the kinetic energy of the cluster ($E_{\text{kin}} < 0.2$ eV/atom³³), the involved chemical binding energy between the cluster and the MgO surface (~0.3 eV per interacting atom for Pd₄³⁴), as well as a negligible Coulomb interaction of the incoming cluster ion and its induced polarization and image charge on the oxide film surface and in the

metal, respectively. Consequently, as the kinetic energies of the impinging clusters correspond to soft-landing conditions ($E_{\text{kin}} \leq 1$ eV)^{35,36} and as the total energy gained upon deposition is at most half of the calculated binding energy of the investigated Pd clusters (ranging from 1.4 to 3.9 eV for Pd₆ to bulk^{37,38}), fragmentation of the clusters induced by the deposition alone is excluded. However, the energetics of the deposition may provide the required activation energy to reach thermodynamically more stable states. For instance, our calculations suggest that the energy gain for the adsorption of two palladium atoms on MgO (~2.6 eV) is larger than the binding energy of the dimer (1.3 eV). Upon impact the cluster ions are neutralized either on defect sites (F-centers) or by charge tunneling through the thin MgO films.³⁹ We deposited only 0.28% of monolayer Pd clusters (1 ML = 2.25×10^{15} clusters/cm²) at 90 K to land them isolated on the surface and to prevent agglomeration on the MgO films.⁴⁰ The support is prepared in situ for each experiment; thin films are epitaxially grown on a Mo(100) surface by evaporating magnesium in a ¹⁶O₂ background⁴¹ and subsequently annealing the oxide film to 1000 K. These films show bulklike properties as observed by low electron energy diffraction (LEED), X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS), and electron energy loss spectroscopy (EELS).⁴⁰ However, small amounts of defects such as steps, kinks, and F-centers are detected by the desorption behavior of small molecules.¹⁷ Depending on the type of defects, a change in the desorption temperature of benzene from small deposited Pd_{*n*} clusters from 200 to 300 K is observed. For the experiments described below, the films were prepared to obtain the high-temperature desorption (300 K) of benzene.

To obtain identical conditions for the study of the cyclotrimerization on different Pd clusters we first exposed, using a calibrated molecular beam doser, the prepared model catalysts at 90 K to an average of five molecules of acetylene per deposited atom. As shown experimentally,⁴² these clusters are saturated with C₂H₂. In a temperature-programmed reaction (TPR) study catalytically formed benzene molecules are detected by a mass spectrometer (BALZERS QMG 421) and monitored as a function of temperature and cluster size. The measured ion signal has been calibrated using the known number of CO molecules desorbing from a Mo(100) single crystal and by taking into account the different ionization cross sections of the two molecules.^{43,44} In addition, Fourier transform infrared (FTIR) spectroscopy is performed in single reflection mode to detect the migration temperature of deposited palladium atoms using CO as a probe molecule.

The calculations were performed using the scalar relativistic version of the linear combination of the Gaussian-type orbitals density functional (LCGTO-DF) cluster method,^{45–47} as implemented in the new parallel program ParaGauss.⁴⁸ The electron density was self-consistently

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determined with the help of the Kohn–Sham procedure using the gradient-corrected functionals for exchange⁴⁹ and correlation.⁵⁰ The MgO surface was modeled by small clusters ([OMg₅]⁸⁺ for a terrace site, [OMg₃]⁴⁺ for a corner site) embedded in a large array of point charges of $\pm 2 e$ to reproduce the Madelung potential.^{51,52} The entire system, ions + point charges, is neutral. Clusters of this type provide a simple, yet reliable representation of surface sites.⁵³ Large orbital basis sets were used: Mg [15s10p1d/6s5p1d], O [13s8p1d/6s5p1d], and Pd [18s13p9d/7s6p4d].³⁴ For the hydrocarbon molecules we used a [9s5p2d/5s4p2d] basis set for C and a [6s2p/3s2p] basis set for H.⁵⁴ Geometry optimizations were carried out by determining analytical gradients of the total energy;⁵⁵ the positions of the surface O ion, the Pd atom, and the hydrocarbon fragments were optimized under the constraint of the site symmetry (C_s and C_{3v}). All other atoms in the substrate cluster are fixed. In general, the computational method adopted here, gradient-corrected DFT with large basis sets, can be considered as highly reliable; in particular, gradient corrections are essential to provide accurate binding energies.⁵⁶ More critical is the model of the MgO substrate that in this study is represented by a very small cluster of ions embedded in point charges. In the past decade several studies have shown that these systems provide the correct physical description of the adsorption processes at oxides.^{57,58} However, one has to be aware of the fact that the limited size of the clusters used here can have some effect on the absolute values of the computed quantities (for instance the geometrical relaxation of an F-center at a corner site is not properly included in our models). Still, given the model character of the study, we believe that the general conclusions are valid and do not depend on the size of the clusters used. Preliminary calculations on larger models support this assumption.⁵⁹

3. Experimental Results

Figure 1 shows the TPR spectra for the cyclotrimerization of acetylene on supported Pd_n ($1 \leq n \leq 30$) clusters. Up to Pd₃, benzene exclusively desorbs at temperatures around 300 K, while a broad feature between 400 and 700 K is observed for cluster sizes up to Pd₈. For Pd₇, an additional desorption peak of benzene is clearly observed at about 430 K. Increasing the cluster size leads to a further intensity increase of this peak. For Pd₈ this feature becomes as important as the peak at 300 K while for Pd₃₀ benzene mainly desorbs around 430 K. We note that on a clean MgO(100) surface no benzene is produced at the same experimental conditions.

By integrating the total area of the TPR spectra shown in Figure 1, the number of catalytically produced benzene molecules per cluster is obtained and shown in Figure 2. Generally, the cluster activity increases with cluster size. Up to Pd₃, an average of one benzene molecule per cluster is produced at 300 K. For Pd_n ($4 \leq n \leq 7$), the total activity increases by a factor of 2, as an additional C₆H₆ molecule is produced between 400 and 700 K. A weak contribution of the desorption peak at 430 K to the total number of produced benzene molecules is observed for Pd₇. For the larger clusters, the increase in the number of C₆H₆ molecules per cluster is only reflected in the intensity of the 430 K desorption peak.

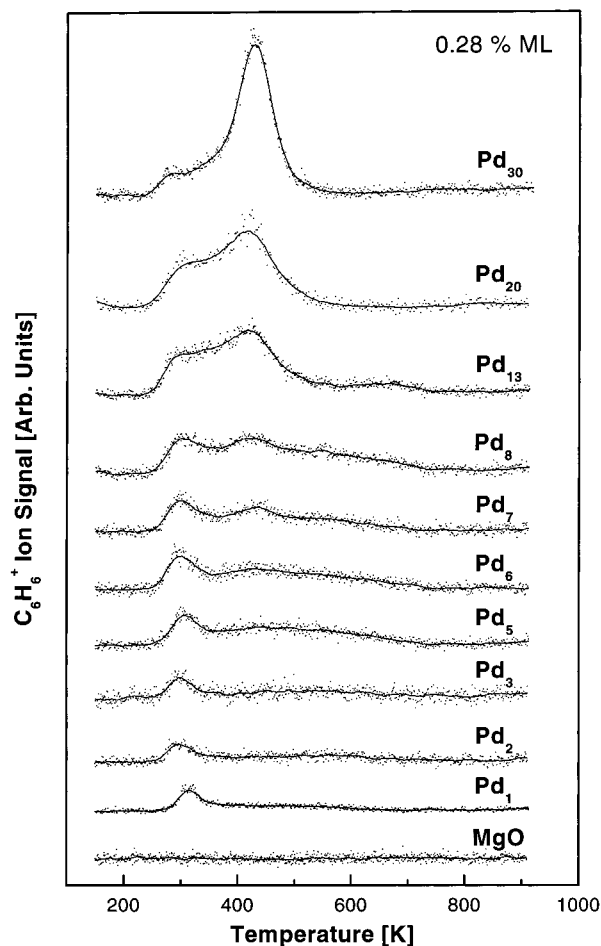


Figure 1. Catalytic C₆H₆ formation for different Pd cluster sizes obtained from temperature-programmed reaction experiments. The bottom spectrum shows that for clean MgO(100) films no benzene is formed. Dots, data; full line, data smoothing with adjacent averaging (25 points). Cluster coverage is 0.28% of a monolayer for all cluster sizes, where one monolayer corresponds to 2.25×10^{15} atoms/cm².

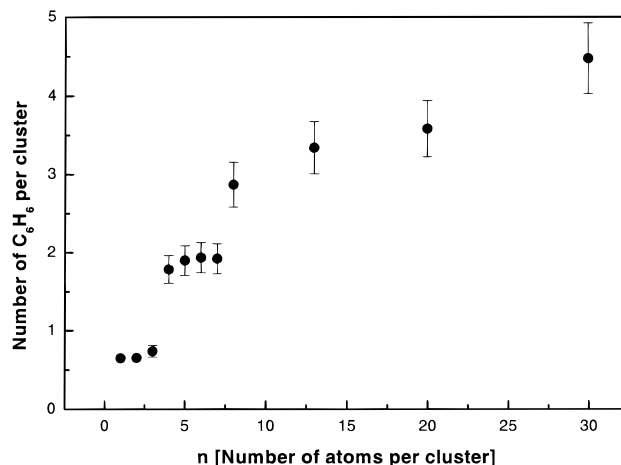


Figure 2. Total number of catalytically produced C₆H₆ molecules per cluster estimated by the integral of the TPR spectra and the number of deposited clusters.

In addition, migration of palladium atoms above 400 K is observed by performing FTIR experiments and using ¹³CO as a probe molecule. At low temperature, a typical frequency for on-top bonded ¹³CO (2010 cm⁻¹) is detected on deposited Pd₁ (Figure 3a). This band disappears at 400 K and a frequency typical for bridge-bonded ¹³CO (1836 cm⁻¹) is observed (Figure

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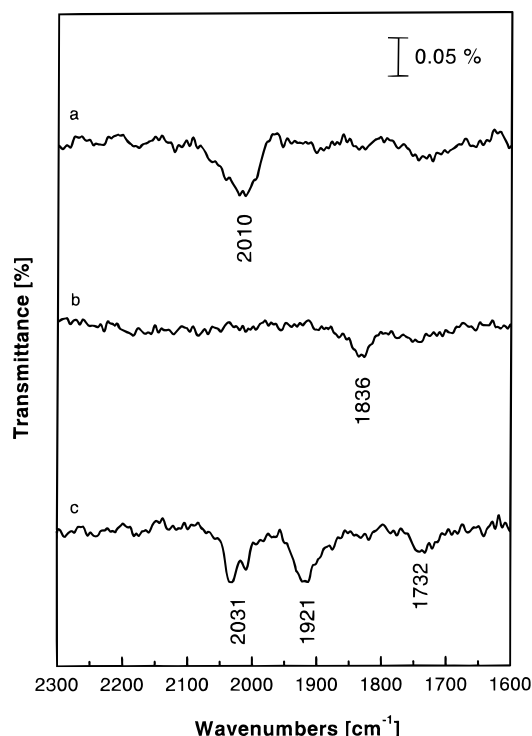


Figure 3. Vibrational frequency of ^{13}CO adsorbed on clean deposited Pd_1 (5% ML) measured at (a) 90 K, (b) after annealing to 400 K, and (c) after annealing to 800 K.

3b). Migration can explain this behavior because on single atoms an on-top frequency (2010 cm^{-1}) is observed while for bridge-bonded ^{13}CO (1836 cm^{-1}) at least a dimer is needed. Moreover, coagulation of atoms upon deposition is excluded, because three different frequencies (2031 , 1921 , and 1732 cm^{-1}), typical for larger Pd clusters,⁶⁰ are observed only after annealing to 800 K (Figure 3c).

4. Computational Results and Discussion

In the TPR experiments desorption of benzene on Pd_n ($1 \leq n \leq 3$) occurs at a temperature of around 300 K and only one C_6H_6 per cluster is produced. This surprising result indicates that already a single palladium atom is sufficient to catalyze the reaction in contrast to suggestions based on single-crystal studies. We therefore investigated theoretically possible reaction mechanisms for the cyclotrimerization of acetylene on small clusters. On a single free Pd atom two C_2H_2 molecules are bound by 1.35 eV/molecule and slightly activated with a HCC angle of 166° . They transform into a C_4H_4 intermediate with an energy gain of 3.9 eV. On free Pd atoms the third acetylene molecule is only weakly bound, at a long distance, 2.6 Å, and practically not activated (Figure 4); thus, cyclotrimerization does not occur. MgO is a basic oxide⁶¹ and the O anions at the surface can act in principle as electron donors. We therefore repeated the calculations for negatively charged Pd atoms carrying a -0.3 or -0.6 net electronic charge. The structure of the C_4H_4 intermediate is not altered, but the third acetylene molecule becomes more activated (e.g. the HCC angle decreases from 177° on neutral $\text{Pd}(\text{C}_4\text{H}_4)$ to 156° on $[\text{Pd}(\text{C}_4\text{H}_4)]^{-0.6}$), which enables formation of benzene.

Motivated by these preliminary results we modeled the experiment in a more realistic way representing the MgO

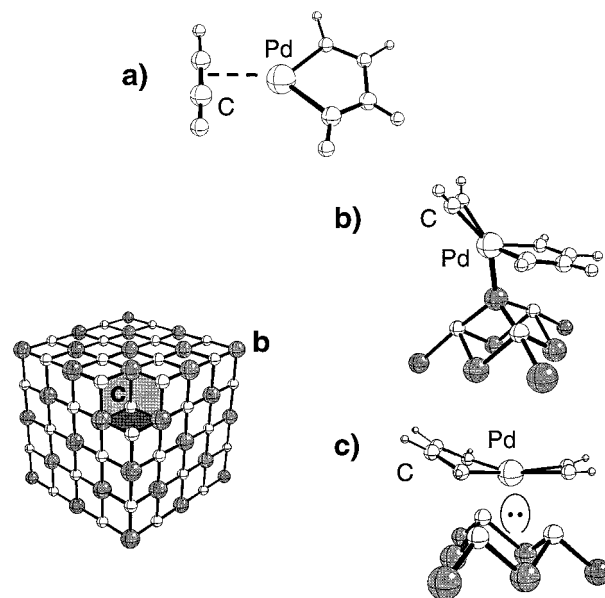


Figure 4. Optimized structures of the complexes (a) $\text{Pd}(\text{C}_4\text{H}_4)(\text{C}_2\text{H}_2)$, (b) $\text{MgO-O}_{3c}\text{-Pd}(\text{C}_4\text{H}_4)(\text{C}_2\text{H}_2)$, and (c) $\text{MgO-F}_{3c}\text{-Pd}(\text{C}_4\text{H}_4)(\text{C}_2\text{H}_2)$. The third O layer in the MgO substrate is represented by point charges (the rest of the point charges are not shown for clarity). The two defect-sites (b and c) are represented in a slab of MgO for illustration.

substrate by a cluster of ions embedded in an array of point charges. We first considered a model of a five-coordinated oxygen ion on the $\text{MgO}(001)$ terrace, O_{5c} , but the Pd atom adsorbed on this site does not further activate the third acetylene molecule; the $\text{Pd}(\text{C}_4\text{H}_4)(\text{C}_2\text{H}_2)$ complex breaks apart without completing the trimerization process. This result, together with a recent experimental and theoretical study on the reactivity of small Au clusters on defect-poor and defect-rich MgO films, which revealed that defect sites are essential for the charging and concomitant catalytic activation of small metal clusters,¹⁷ strongly suggests that defect sites are also essential for the activation of small palladium clusters. We therefore considered a three-coordinated corner oxygen site, O_{3c} , and an oxygen vacancy (F-center) located at a corner site, F_{3c} , as these defects are the most active ones in terms of their basic behavior. (Recent experimental and theoretical studies have shown that F centers at low coordinated sites exist and are more stable than those at terraces.^{62–65})

Pd atoms bind to oxygen ions at corner sites at a bond distance of 1.989 Å with a binding energy of 1.7 eV, a value about 50% larger than that for terrace sites. The supported $\text{Pd}(\text{C}_4\text{H}_4)$ complex binds the third acetylene molecule by 0.48 eV and activates it much more than a neutral or negatively charged Pd atom, as shown by the longer C–C bond (Table 1) and the small HCC angle (Table 1). Hence, the oxide support considerably increases the charge transfer from the Pd atom to the adsorbed acetylene and transforms the “inert” free Pd atom into an active catalyst. During this activation the flow of electronic charge from the supported Pd atom to the adsorbed molecule is larger for corner than for step or terrace sites. This is clearly shown by a decomposition⁶⁶ of the total energy and of the dipole

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Table 1. Calculated Properties of Acetylene Bound to a Free or Supported Pd(C₄H₄) Complex

	Pd	Pd ^{-0.6}	(MgO)O _{3c} -Pd	(MgO)F _{3c} -Pd
<i>r</i> (Pd–C), ^a Å	2.617	2.257	2.038	2.075
<i>r</i> (C–C), ^a Å	1.216	1.256	1.304	1.315
α(HCC), ^a deg	177	156	142	139
Δ <i>E</i> , ^b eV	3.58	2.91	4.04	2.42
<i>D</i> _{es} , ^c eV	0.76	0.23	0.32	0.06
<i>z</i> (Pd–C ₆ H ₆), ^d Å	2.024	2.107	2.193	2.306

^a Geometrical parameters of a third acetylene molecule; *r*(C–C) in free acetylene is 1.210 Å. ^b Energy gain for the reaction C₄H₄ + C₂H₂ → C₆H₆ on the Pd complex. ^c Dissociation energy of benzene from the Pd complex. ^d Distance between the center of the benzene molecule and the Pd atom.

moment into the sum of individual mechanisms (Pauli repulsion, charge transfer, polarization, etc.) performed at the Hartree–Fock level: for a Pd bound at a corner site, the charge flow from the substrate to the adsorbed hydrocarbon is about four times larger than that for a free atom and twice as large as that for a terrace site. This is consistent with the higher basicity of the oxygen ions at low coordinated sites due to the lower Madelung potential.⁶⁷ On the activated Pd atom the (MgO)-O_{3c}-Pd(C₄H₄)(C₂H₂) surface complex evolves into an adsorbed benzene with an energy gain of 4.08 eV. This large energy gain is mainly related to the aromaticity of the benzene ring formed; the reaction product is only weakly bound to the MgO(O_{3c})-Pd complex, 0.3 eV, which explains the rather low desorption temperature. In addition, bonding of benzene to an activated Pd atom and to different MgO sites is similar and therefore spill-over of benzene to the support is likely.

We also considered an F-center located at a three-coordinated corner site, F_{3c}. This corresponds to two electrons trapped at the site left by the missing O atom.⁶² At this defect site, a Pd atom is bound by 4.3 eV, i.e., much more strongly than on an O_{3c} site. This supported atom is even more efficient than a Pd on a O_{3c} in activating the adsorbed acetylene, which is bound by 2.63 eV. In fact, the complex MgO(F_{3c})-Pd(C₄H₄)(C₂H₂), Figure 4, shows a larger distortion and a stronger interaction of the third C₂H₂ molecule, Table 1. At the moment one cannot establish which defect site is more active in promoting the reaction,⁶⁸ but the present results indicate that both low-coordinated O²⁻ ions and F-centers (not necessarily located at a corner site) can act as basic sites on the MgO surface. These results show that supported Pd atoms on defect sites not only activate the cyclization reaction but also favor the desorption of benzene, as shown by the longer Pd–C₆H₆ distance and the smaller adsorption energy (Table 1).

Deposited dimers also provide an interesting scenario for the cyclization reaction. Free Pd dimers are able to adsorb two acetylene molecules, forming the intermediate C₄H₄. In contrast to free atoms, dimers add and activate a third acetylene molecule. Thus, they feature enough electron density to promote the reaction even without an active role of the substrate. However, the stability of two Pd atoms bound through a covalent bond of 1.3 eV/atom to terrace O ions is larger than the metal–metal interaction of gas-phase Pd₂, 1.3 eV. In a very recent study on the bonding mode and the possible orientations of Pd₂ on a nondefective MgO(001) surface we showed that from a purely thermodynamic point of view two isolated Pd atoms adsorbed

on MgO are more stable than an adsorbed dimer.⁶⁹ In view of the experimental results, that only one benzene molecule is produced per deposited dimer, we suggest that one atom is activated and adsorbed on a defect site, while the other one is adsorbed on a terrace site and therefore not activated. We are now testing this argument by increasing the defect density on our MgO films. The observed migration of Pd atoms above 400 K (Figure 3) suggests that for small Pd_n clusters (4 ≤ *n* ≤ 6) on MgO(100) the broad feature observed between 400 and 700 K is related to migration. Here C₄H₄ may be formed on small clusters and after migration this intermediate reacts with an acetylene molecule adsorbed on another cluster.

On larger clusters (Pd_n with 7 ≤ *n* ≤ 30) a distinct production of benzene at 430 K is observed. This feature is typical for the production of benzene on the surface of large clusters where the three C₂H₂ molecules are bound to different sites, e.g., three 3-fold sites, the most stable configuration for Pd(111) single crystals. In addition, distinct desorption of benzene at 430 K is first observed for Pd₇, suggesting the heptamer to be the critical cluster size for that mechanism. Up to Pd₃₀, the number of C₆H₆ molecules per cluster, mainly produced at 430 K, increases as the number of adsorption sites on the clusters increases with cluster size. The higher desorption temperature of benzene for this reaction mechanism may be rationalized with a transition from two-dimensional to three-dimensional cluster shapes. Theoretical work⁶⁷ on Ni clusters supported on model systems for Al₂O₃ has shown that one-layer and two-layer Ni clusters behave differently: while the metal layer in direct contact with the oxide substrate is electronically perturbed, the second metal layer behaves very similarly to an unsupported Ni cluster. Work is in progress to determine the adsorption energy of benzene on one- and two-layer Pd clusters on MgO and the preferred shape and orientation of small Pd clusters on MgO. We recently showed that a Pd tetramer, which assumes a tetrahedral shape in the gas phase, maintains the same structure and a similar degree of s–d hybridization when deposited on the nondefective MgO surface.⁶⁹

5. Conclusion

The investigated model catalysts of size-selected Pd_n (*n* ≤ 30) clusters supported on MgO(100) thin films exhibit a pronounced size effect for the cyclotrimerization of acetylene to benzene for a single-pass heating cycle. For small clusters, up to Pd₃, benzene is exclusively produced at 300 K whereas for the heptamer the formation of benzene at a temperature of about 430 K starts to evolve. Surprisingly, already a single Pd atom catalyzes the production of benzene. Density functional calculations showed that single Pd atoms can be catalytically activated only when adsorbed on basic defect sites of MgO and when charge is transferred to the metal atom. For the larger clusters, the cyclotrimerization occurs mainly at a temperature of 430 K. It is suggested that in this mechanism benzene is formed in a similar geometry as on Pd single crystals or large Pd particles where 3-fold hollow sites are most favorable for C₂H₂ adsorption. We showed experimentally that the critical ensemble for this mechanism consists of seven atoms.

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