

Role of Surface Defects in the Activation of Supported Metals: A Quantum-Chemical Study of Acetylene Cyclotrimerization on Pd₁/MgO

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We report results of first principle density functional calculations on the catalytic activity of isolated Pd atoms deposited on different MgO surface sites. The reaction of interest is the cyclization of acetylene to benzene, $3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$. Experimentally, it has been observed that the reaction is catalyzed by size-selected Pd clusters and that even a single Pd atom deposited on MgO is enough for the reaction to occur. In this theoretical study we have analyzed in detail the role of the support. It is found that a gas-phase Pd atom is not active in promoting the reaction as it has not enough electron density to bind and activate three acetylene molecules. The reaction, however, occurs when Pd is bonded to low-coordinated oxygen anions of the surface, located at sites such as steps and corners. Oxygen anions on (001) terraces, in fact, are not a sufficiently good electron donor to increase the electron density on the metal. Another group of surface defects which play a role in the activation of the Pd atom are F centers, oxygen vacancies with two trapped electrons. These defect centers, independently of their location, terrace, edge, or corner, are very strong “basic” sites: they efficiently transfer electronic charge to the adsorbed metal atom and thus improve its catalytic properties. This study demonstrates the importance of morphological defects and anion vacancies at the metal–oxide interface and the noninnocent role of the substrate in catalysis by supported metal particles.

1. Introduction

The role of the support in heterogeneous catalysis is a subject of continuous discussion and interest in surface chemistry.^{1–3} It is often assumed that the support, usually an insulating oxide such as SiO₂, Al₂O₃, or MgO, simply acts to disperse the catalytically active metal particles without influencing their electronic properties. Under some circumstances, strong metal–support interactions have been observed and explained in terms of drastic changes in the electronic structure of the metal catalyst due to the metal–oxide interface bond.¹ New techniques which allow the deposition of size-selected metal clusters on thin oxide films in ultra-high-vacuum (UHV) conditions open new perspectives for the investigation of the metal–support interaction.^{4–6} Recently we have presented experimental evidence that small mass-selected Pd clusters deposited on MgO thin films exhibit very specific catalytic activity and selectivity.⁷ The reaction considered here is the cyclization of acetylene to benzene, $3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$. It has been widely studied on single-crystal surfaces from UHV conditions (10^{-12} – 10^{-8} atm) to atmospheric pressure (10^{-1} –1 atm).^{8–11} A Pd(111) surface is the most reactive one,^{12,13} and it has been shown unambiguously that the reaction proceeds through the formation of a stable C₄H₄ intermediate, resulting from addition of two acetylene molecules.¹⁴ This intermediate has been characterized experimentally^{15–17} and theoretically,¹⁸ and its structure is now well established. Once

the C₄H₄ intermediate is formed, it can add a third acetylene molecule to form benzene that then desorbs from the surface at a temperature of about 230 K.^{8,9} It is believed that in this case the benzene coverage is high and that the molecules are forced into a weaker binding configuration with the molecular axis tilted with respect to the Pd(111) surface. At low coverage and on flat surfaces the benzene molecule lies parallel to the surface and desorbs at 500 K.^{8,9} Surface science studies have shown that the existence of an ensemble of three 3-fold sites on the Pd(111) surface is necessary for the reaction to occur,^{12,19} and that this can explain the surface sensitivity of the reaction. Very similar reaction patterns have also been observed on Al₂O₃-supported Pd particles of a few nanometers size as they exhibit (111) and (100) microfacets on their surface.^{10,20}

In view of the surface sensitivity of the reaction, it is rather surprising that in the experiments on size-selected Pd clusters on MgO thin films even a single Pd atom induces the acetylene cyclization.⁷ In a preliminary series of calculations we have shown that this is connected to the fact that the metal atom interacts with point defects at the surface of MgO with consequent increase of the charge density around the Pd atom which becomes an active single-atom catalyst.⁷ In a similar way, in coordination chemistry, one can modify the activity of a given metal center by changing the ligands. In our previous study, however, only defects of one type, three-coordinated oxide anions and the corresponding vacancies, have been considered.⁷ Here we present the cyclization reaction in more detail, looking at various types of morphological defects as well as at vacancy sites, and performing an accurate analysis of the electronic effects involved in the metal–support interaction. To this end,

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we have carried out cluster model density functional (DF) calculations on cluster models of the MgO support. The results provide a more quantitative measure of the degree of activation of Pd deposited on low-coordinated oxygen anions at terrace, edge, and corner sites, as well as on neutral oxygen vacancies, the F centers, located at the same positions.

2. Computational Method

The DF calculations have been carried out with the help of the scalar-relativistic variant of the linear combination of Gaussian-type orbitals density functional method (LCGTO-DF)^{21,22} as implemented in the new program ParaGauss for parallel computing.^{23,24} All-electron Gaussian-type basis sets were employed to construct the Kohn–Sham orbitals: (15s 10p 1d) → [6s 5p 1d] for Mg, (13s 8p 1d) → [6s 5p 1d] for O, (18s 13p 9d) → [7s 6p 4d] for Pd. For C and H we used a [9s 5p 2d] → [5s 4p 2d] and a [6s 2p] → [3s 2p] basis set, respectively.²⁵ In this work, we used the gradient-corrected BP functional (Becke's exchange functional²⁶ in combination with Perdew's correlation functional²⁷) self-consistently. For further details about the computational aspects, see for instance ref 28.

The MgO(001) surface was represented by cluster models,^{29,30} an approach which has been found to reproduce in a sufficiently accurate way the electronic structure and the binding properties of surface complexes.^{2,31} Due to the highly ionic nature of MgO, the truncation of the lattice in cluster calculations implies the use of an external field to represent the long-range Coulomb potential. The model clusters considered have been embedded in arrays of point charges (PC = ±2 e) in order to reproduce the correct Madelung potential at the adsorption site under study.³² The complete models, ions and PCs taken together, are electrically neutral. The positions of all substrate atoms and PCs were kept fixed at bulk-terminated values of MgO, with a measured bulk Mg–O distance of 2.104 Å.³³ Previous studies^{34–36} have demonstrated that the use of PCs for embedding significantly affects the calculated adsorption properties when the positive PCs are nearest neighbors to the highly polarizable oxygen anions of the clusters. In that case, an artificial polarization of the oxygen anions at the cluster borders results; however, this artifact can be essentially eliminated by surrounding the anions with total ion model potentials (TIMPs)³⁵ of Mg²⁺ or “real” Mg²⁺ cations instead of positive PCs. Test calculations obtained using TIMPs or real Mg²⁺ ions give very similar results.³⁶ The morphological defects and the F centers have been described by two sets of cluster models. In a minimum model of surface anions we have considered explicitly only the O anion and the first shell of Mg cations, OMg₅, OMg₄, and OMg₃, for terrace, edge, and corner sites, respectively. The rest of the crystal is represented by PCs. The same models, with the O atom removed, have also been used to represent the corresponding O vacancies. Since these clusters are terminated by Mg²⁺ cations, TIMPs have not been included. However, given the small size of these clusters, we have considered another group of models for F centers where the next shell of O anions is explicitly included, namely Mg₃O₆ (F_{3C}), Mg₄O₆ (F_{4C}), and Mg₅O₁₂ (F_{5C}). The clusters are embedded in TIMPs and arrays of 980, 1666, and 540 PCs for corner, edge, and terrace sites, respectively. The two sets of clusters provide very similar answers, and only the results of the larger models are reported. The positions of the surface oxide anion, of the supported metal atom, and of the adsorbed C₂H₂, C₄H₄, and C₆H₆ molecules, Figures 1–4, have been optimized using analytical energy gradients.³⁷

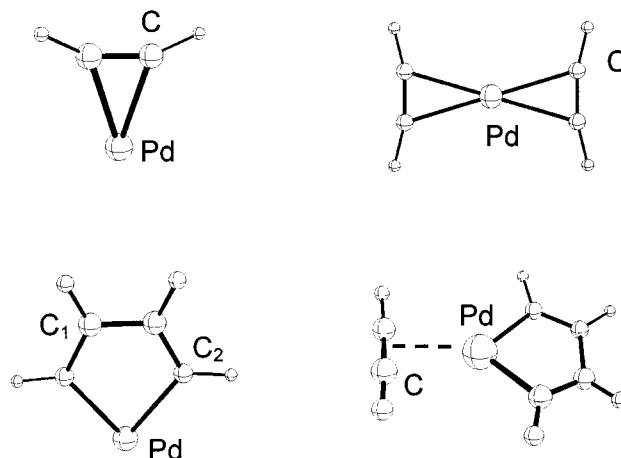


Figure 1. Optimal structure of the complexes Pd(C₂H₂), Pd(C₂H₂)₂, Pd(C₄H₄), and Pd(C₂H₂)(C₄H₄).

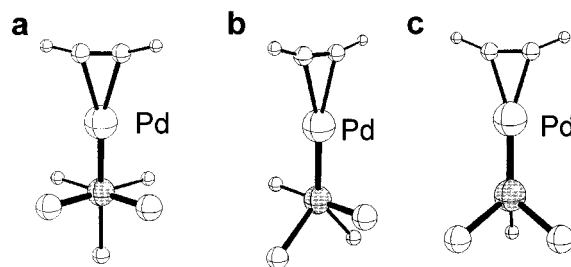


Figure 2. Models of a C₂H₂ molecule bound to a Pd atom supported on (a) a five-coordinated O^{2−} anion at a terrace site, (b) a four-coordinated O^{2−} anion at an edge site, and (c) a three-coordinated O^{2−} anion at a corner site. The clusters are embedded in a large array of point charges (not shown); the geometry optimizations have been performed at the HF level.

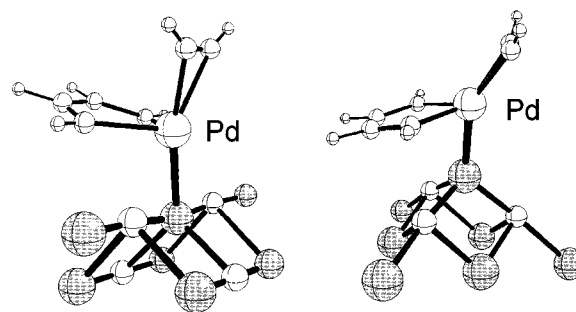
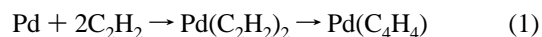


Figure 3. Optimal structure of a Pd(C₂H₂)(C₄H₄) complex supported on a four-coordinated oxygen anion at an edge site (left), and on a three-coordinated oxygen anion at a corner site (right). The cluster is surrounded by a large array of point charges (not shown). The external shell of O anions shown in the figure has been treated as PCs with $q = -2$ e.

3. Results and Discussion

3.1. Isolated Pd Atom. The possibility to catalyze the acetylene trimerization depends critically on the ability of the metal center to coordinate and activate two C₂H₂ molecules, Figure 1, and then to bind the C₄H₄ intermediate according to the reaction



The activation of the acetylene molecules is easily monitored, for instance, by the deviation from linearity of the HCC angle due to a change of hybridization of the C atom from sp to sp², or by the elongation of the C–C distance, $d(\text{C}–\text{C})$, as a consequence of the charge transfer from the metal 4d orbitals

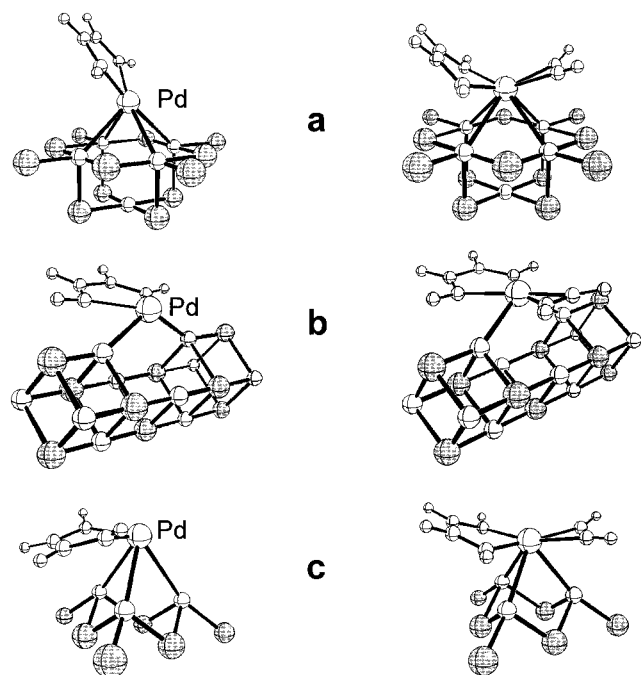


Figure 4. Optimal structure of $\text{Pd}(\text{C}_4\text{H}_4)$ (left) and $\text{Pd}(\text{C}_2\text{H}_2)(\text{C}_4\text{H}_4)$ (right) complexes supported on (a) an $\text{F}_{3\text{C}}$ defect center at a terrace site, (b) an $\text{F}_{4\text{C}}$ defect center at an edge site, and (c) an $\text{F}_{3\text{C}}$ defect center at a corner site. The cluster is surrounded by a large array of point charges (not shown).

TABLE 1: Properties of $\text{Pd}(\text{C}_2\text{H}_2)$, $\text{Pd}(\text{C}_2\text{H}_2)_2$, and $\text{Pd}(\text{C}_4\text{H}_4)$ Complexes^a

	$\text{Pd}-\text{C}_2\text{H}_2$	$\text{Pd}-(\text{C}_2\text{H}_2)_2$	$\text{Pd}-\text{C}_4\text{H}_4$
$d(\text{C}-\text{C}),^b \text{\AA}$	1.271	1.238	1.350
$d(\text{C}-\text{Pd}), \text{\AA}$	2.043	2.192	1.994
$\angle(\text{HCC}), \text{deg}$	154.3	166.4	
$\text{BE},^c \text{eV}$	1.81	2.71	3.93

^a DF results. ^b Calculated result for free C_2H_2 : $d(\text{C}-\text{C}) = 1.210 \text{\AA}$.
^c Binding energy computed as: $E(\text{Pd}) + nE(\text{C}_2\text{H}_2) - E[\text{Pd}(\text{C}_2\text{H}_2)_n]$.

to the empty π^* orbital of acetylene.¹⁸ This process has been considered by optimizing the geometry of one and two acetylene molecules coordinated to an isolated Pd atom, and of the corresponding $\text{Pd}(\text{C}_4\text{H}_4)$ complex, Figure 1 and Table 1. The C_4H_4 intermediate is quite strongly bound to the Pd atom and is 1.2 eV more stable than two adsorbed acetylene molecules, Table 1. A similar result has been obtained for the $\text{Pd}(111)$ surface.¹⁸ The level of activation of acetylene is clearly larger when a single C_2H_2 is adsorbed, consistent with the idea that the electron density on the metal is essential for promoting the molecular activation.

The following step, $\text{C}_4\text{H}_4 + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$, requires the capability of the metal center to coordinate and activate a third acetylene molecule according to the reaction



However, the third C_2H_2 molecule interacts very weakly with $\text{Pd}(\text{C}_4\text{H}_4)$ with a binding of 0.3 eV (actually an overestimate because of the occurrence of the basis set superposition error, BSSE).³⁸ The structure of the third molecule is not deformed compared to the gas phase, with $d(\text{C}-\text{C}) = 1.216 \text{\AA}$ and a HCC angle of 177° . In reality, the molecule may be bound to the $\text{Pd}(\text{C}_4\text{H}_4)$ complex by dispersion forces (not described by the BP exchange-correlation approximation) and its distance from the Pd atom is indeed very long, 2.617 \AA . This result indicates

TABLE 2: Properties of a C_2H_2 Molecule Interacting with the Complex $\text{Pd}^q(\text{C}_4\text{H}_4)$ as a Function of the Charge q^a

	$\text{Pd}^{+0.6}$	$\text{Pd}^{+0.3}$	Pd^0	$\text{Pd}^{-0.3}$	$\text{Pd}^{-0.6}$
$d(\text{C}-\text{C}),^b \text{\AA}$	1.217	1.216	1.216	1.228	1.256
$d(\text{C}-\text{Pd}), \text{\AA}$	2.582	2.586	2.617	2.454	2.257
$\angle(\text{HCC}), \text{deg}$	175.7	176.3	177.3	171.7	156.3
$\text{BE},^c \text{eV}$	0.60	0.44	0.30	0.41	0.66

^a DF results. ^b Calculated result for free C_2H_2 : $d(\text{C}-\text{C}) = 1.210 \text{\AA}$.
^c Binding energy computed as $\text{BE} = E[\text{Pd}(\text{C}_4\text{H}_4)] + E(\text{C}_2\text{H}_2) - E[\text{Pd}(\text{C}_4\text{H}_4)(\text{C}_2\text{H}_2)]$.

that an isolated Pd atom is not a catalyst for the cyclization process, at variance with the experimental observation for Pd_1/MgO .⁷

Therefore the role played by the support becomes an issue. In recent years several experimental and theoretical studies have been dedicated to the interaction of metal atoms and clusters with oxide surfaces and in particular with MgO .^{28,39–42} It is now well established that the preferred sites for metal binding are the oxygen anions of the surface.^{39–43} The Pd–MgO bonding, however, is not characterized by a pronounced charge transfer and is described as covalent polar.²⁸ Thus far, only regular adsorption sites have been considered and the bonding mode and character at defect or low-coordinated sites has been investigated in much less detail.^{44,45} In this respect one can formulate two hypotheses. One of them states that the surface oxygen anions of the MgO surface still have some oxidizing power to deplete charge from the metal atom. The other possibility is that the O anions are fully reduced, O^{2-} , and donate charge to the metal atom, thus leading to electron-enriched species (the surface acts as a Lewis base). In the two cases one would end up with positively or negatively charged supported Pd atoms, respectively. In principle, both situations can lead to an activation of the supported metal. In fact, the bonding of unsaturated hydrocarbons to metal complexes and metal surfaces is classically described in terms of σ donation from a filled bonding level on acetylene to empty states on the metal and π back-donation from the occupied d orbitals on the metal to empty antibonding π^* orbitals of the ligand.^{46,47} Both mechanisms result in a weakening of the C–C bond and a distortion of the molecule. We have considered a series of Pd atoms whose net charge q has been artificially augmented or decreased from 0.6 e to -0.6 e; this is possible using a fractional occupation number technique, Table 2.²¹ We have then considered the structure of the complex $\text{Pd}^q(\text{C}_2\text{H}_2)(\text{C}_4\text{H}_4)$ as a function of q . While this is not a realistic model, it provides a general trend and a simple correlation.

The presence of a charge on Pd, either positive or negative, reinforces the bonding of acetylene to the $\text{Pd}(\text{C}_4\text{H}_4)$ complex, Table 2; however, only for $q < 0$ (electron-rich atom) is a substantial activation of the third acetylene molecule observed. Furthermore, the value of the net charge has to be relatively large, since $\text{Pd}^{-0.3}(\text{C}_4\text{H}_4)$ very weakly modifies the linear shape of the third acetylene and its C–C distance. For $q = -0.6$ e the molecule becomes substantially activated. This result shows that the increase of the electron density on Pd is the key mechanism to augment the catalytic properties of the metal atom.

3.2. Supported Pd Atoms. To establish the role of the regular and low-coordinated surface anions of MgO in modifying the properties of a supported Pd atom, we have considered three simple models. They represent five-, four-, and three-coordinated O anions at terrace, edge, and corner sites, respectively; a $\text{Pd}(\text{C}_2\text{H}_2)$ complex has been added on top of these oxygen atoms, Figure 2 and Table 3. Given the qualitative nature of the analysis, the Pd–O distance has been fixed to 2.2 \AA and only

TABLE 3: Properties of Free and MgO-Supported Pd(C₂H₂) Complexes^a

	Pd(C ₂ H ₂)	MgO terrace	MgO edge	MgO corner
		OMg ₅ /Pd(C ₂ H ₂)	OMg ₄ /Pd(C ₂ H ₂)	OMg ₃ /Pd(C ₂ H ₂)
<i>d</i> (C–C), Å	1.201	1.212	1.219	1.237
<i>d</i> (C–Pd), Å	2.452	2.204	2.158	2.075
∠(HCC), deg	173.8	167.8	164.2	157.4
CT ^b C ₂ H ₂ → Pd Δ <i>E</i> , eV	0.16	0.40	0.46	0.55
CT ^b C ₂ H ₂ → Pd Δ <i>μ</i> , D	0.34	0.59	0.65	0.59
CT ^b Pd → C ₂ H ₂ Δ <i>E</i> , eV	0.34	0.97	1.20	2.03
CT ^b Pd → C ₂ H ₂ Δ <i>μ</i> , D	−0.72	−1.78	−2.16	−3.14

^a HF results. The distance between the Pd atom and the MgO oxygen center has been kept fixed at 2.2 Å in all calculations. See also Figure 2.

^b CSOV results. Variation in the total interaction energy, Δ*E*, and of the *z*-component of the dipole moment Δ*μ*, associated to charge transfer, CT, mechanisms.

the geometry of acetylene has been fully optimized, Table 3. The results have been compared with those for an isolated Pd(C₂H₂) complex. Differently from the other results presented in this paper, these calculations have been carried out at the Hartree–Fock level in order to apply the constrained space orbital variation, CSOV, method.^{48,49} With the CSOV method one is able to decompose the interaction energy of the system into a sum of various bonding contributions, such as intraunit polarization and charge transfer, Table 3. Recently, examples of CSOV decompositions performed at the HF and DFT level have been reported;^{50,51} they have shown that the relative weight of the various contributions to the bonding from HF and DFT calculations is similar.

When Pd is deposited on MgO, the activation of C₂H₂ is much more efficient than for an isolated Pd atom. The structural distortion of adsorbed C₂H₂ follows the trend corner > edge > terrace > free atom, Table 3. The values of Δ*E*, the change in interaction energy, and of Δ*μ*, the change in dipole moment, associated with the charge-transfer mechanisms provide a more quantitative measure of the role of the substrate. In particular, since the nuclei are fixed during the CSOV decomposition, Δ*μ* measures the flow of charge in one or the other direction. A positive Δ*μ* corresponds to an electron flow from acetylene to Pd and vice versa. The contribution of the charge transfer from acetylene to Pd or Pd₁/MgO, the σ donation in the Dewar–Chatt–Duncanson model,^{46,47} is similar for the four cases, Table 3, and is much smaller than the charge transfer in the other direction, i.e., from Pd or Pd₁/MgO to acetylene. The donor capability increases in the order terrace < edge < corner, the same order found for the deformation of the acetylene molecule.

This qualitative analysis shows unambiguously that (a) the substrate plays a direct role in the modification of the properties of the supported Pd atom, and (b) low-coordinated sites are more active than the regular terraces. This is consistent with the idea that the degree of surface basicity in MgO is larger for the low-coordinated anions because of the lower Madelung potential at these sites.⁵²

In principle there are several defect sites which can be active in promoting the catalytic activity of a deposited Pd atom. The surface of polycrystalline MgO presents in fact a great variety of irregularities⁵³ such as morphological defects, anion and cation vacancies,^{54,55} divacancies,⁵⁶ and impurity atoms. Each of these defects can then have a different coordination number and be located at terraces, steps, kinks, corners, etc. Recent studies have shown that even MgO thin films deposited on a conducting substrate under controlled conditions are not completely defect free, as shown by the different adsorption properties of CO on MgO thin films and single-crystal surfaces.⁵⁷

It is therefore difficult to answer the question of which defect sites of the MgO surface are more likely involved in the

acetylene trimerization. To contribute to a clarification of the role of defects, we have considered the structure and stability of Pd atoms, Pd(C₄H₄), and Pd(C₂H₂)(C₄H₄) complexes on various regular and defect sites at the MgO surface, in particular O sites, Figure 3, and neutral oxygen vacancies (the F centers), Figure 4. Recent theoretical^{58,59} and experimental⁵⁵ studies suggest that F centers form preferentially at low coordinated sites such as kinks and corners. F_s centers, where the subscript *s* indicates the location of the defect at the surface, are characterized by the presence of trapped electrons in the cavity.⁶⁰ The electron localization is shown, for instance, by electron density plots.⁶⁰ If only one electron is present, one is dealing with a paramagnetic F_s⁺ center whose electronic structure and properties have been discussed in a series of recent papers.^{54,55,58,60} Because of its positive charge, the F_s⁺ centers are not as good candidates as nucleophilic sites as the neutral F centers and have not been considered in this work. In the following we use the notation F_{3C}, F_{4C}, and F_{5C} to indicate F centers located at corner, edge, and terrace sites, respectively.

We consider first the adsorption energy of an isolated Pd atom on the various sites considered (DF results with BP exchange–correlation functional). On a flat terrace, OMg₅, the binding energy is 1.30 eV; it is slightly higher on edge and corners, 1.71 eV for OMg₄ and 1.70 eV for OMg₃. Much stronger Pd₁/MgO interactions are found on F centers: 3.48 eV on F_{5C}, 3.87 eV on F_{4C}, and 4.33 eV on F_{3C}. The stronger bonding in the latter cases arises from the delocalization of the trapped electrons into the 5s orbital of Pd which is empty in the atomic ground state (4d¹⁰5s⁰).^{44,61} Thus, Pd atoms deposited on MgO have a greater chance to be stabilized at defect sites where the bonding is stronger.

Next, we consider the formation of the surface complexes at O anions, starting with the five-coordinated oxygens at the (001) terraces. The addition of the two acetylene molecules to OMg₅/Pd results in a stable complex which then evolves in a OMg₅/Pd(C₄H₄) species. However, the addition of the third acetylene molecule does not occur. The situation is reminiscent of that of an isolated Pd atom where the third acetylene is weakly bound by dispersion forces but here other bonding mechanisms compete, for instance the direct interaction of C₂H₂ with the MgO surface. Therefore, the complex is unstable and acetylene does not bind to OMg₅/Pd₁(C₄H₄). Thus, even if Pd atoms exist at the MgO terraces, they are not active in promoting the cyclization reaction. On the other hand, if one considers the formation of Pd(C₄H₄) on four- and three-coordinated oxygens, Table 4, and the consequent addition of the third acetylene molecule, Table 5, one observes the formation of a stable complex, although the interaction is weak, 0.32 eV for OMg₄/Pd(C₂H₂)(C₄H₄) and 0.48 eV for OMg₃/Pd(C₂H₂)(C₄H₄), Table 5. The activation of the third acetylene is much more pronounced for the corner site, Table 5, where the C–C bond is elongated

TABLE 4: Properties of the Complex Pd(C₄H₄) Supported on Various MgO Sites^a

MgO site	OMg ₄	OMg ₃	F _{5C}	F _{4C}	F _{3C}
<i>d</i> (C ₁ –C ₁), Å	1.453	1.464	1.464	1.485	1.422
<i>d</i> (C ₂ –C ₁), Å	1.367	1.354	1.358	1.351	1.406
<i>d</i> (C ₂ –Pd), Å	1.999	2.004	2.038	2.193	1.997
<i>∠</i> (C ₂ C ₁ C ₁), deg	113.4	123.5	112.7	123.9	112.8
BE, ^b eV	2.52	3.80	1.72	1.95	2.12

^a DF results; see Figure 1 for definitions. ^b Binding energy computed as BE = 2*E*(C₂H₂) + *E*(Pd₁/MgO) – *E*[Pd₁(C₄H₄)/MgO].

TABLE 5: Properties of the Complex Pd(C₂H₂)(C₄H₄) Supported on Various MgO Sites^a

MgO site	OMg ₄	OMg ₃	F _{5C}	F _{4C}	F _{3C}
<i>d</i> (C ₁ –C ₁), Å	1.490	1.496	1.465	1.466	1.466
<i>d</i> (C ₂ –C ₁), Å	1.352	1.355	1.362	1.357	1.366
<i>d</i> (C ₂ –Pd), Å	2.142	2.140	2.115	2.136	2.145
<i>d</i> (C–C), ^b Å	1.275	1.304	1.310	1.314	1.315
<i>d</i> (C–Pd), Å	2.083	2.038	2.070	2.087	2.080
<i>∠</i> (HCC), deg	152.0	142.0	139.9	138.0	138.4
BE ^c , eV	0.32	0.48	1.10	2.39	2.73

^a DF results; see Figure 1 for definitions. ^b Calculated result for free C₂H₂: *d*(C–C) = 1.210 Å. ^c Binding energy computed as BE = *E*[Pd₁(C₄H₄)/MgO] + *E*(C₂H₂) – *E*[Pd₁(C₄H₄)(C₂H₂)/MgO].

TABLE 6: Properties of the Complex Pd(C₆H₆) Supported on Various MgO Sites^a

	unsupported	OMg ₄	OMg ₃	F _{5C}	F _{4C}	F _{3C}
<i>d</i> (C–C), ^b Å	1.417	1.410–1.414 ^c	1.412	1.411	1.413	1.409
<i>d</i> (C–Pd), Å	2.471	2.564	2.608	2.609	2.603	2.702
<i>z</i> (C ₆ H ₆), ^d Å	2.024	2.142	2.193	2.198	2.189	2.306
BE, ^e eV	0.76	0.56	0.32	0.32	0.34	0.06
Δ <i>E</i> , ^f eV	3.58	4.76	4.04	4.61	2.96	2.42

^a DF results. ^b Calculated result for free C₆H₆: *d*(C–C) = 1.401 Å. ^c The C_{2v} symmetry of this site leads to a distorted C₆H₆ molecule. ^d Distance of Pd from the center of the benzene ring. ^e Binding energy computed as BE = *E*(S) + *E*(C₆H₆) – *E*[S(C₆H₆)]; S = Pd or Pd₁/MgO. ^f Energy difference for the process Pd(C₄H₄)(C₂H₂) → Pd(C₆H₆).

to 1.304 Å and the HCC angle is 142°. Thus, differently from the terrace sites, the O anions at low-coordinated defects promote the catalytic activity of supported Pd atoms.

We come now to the F centers. They all show a similar activity, with formation of a stable Pd(C₄H₄) complex and stabilization of the third acetylene molecule, Table 5; the strength of the bonding of C₂H₂ to the supported Pd(C₄H₄) complex is larger than for the morphological defects and becomes quite large, 2.73 eV, for an F_{3C} center, Table 5. The degree of activation is comparable in the three cases, with C–C distances of about 1.31 Å and HCC angles of about 140°. The different strength of the bond of the third acetylene molecule can have consequences on the barrier to benzene formation and on the kinetics of the process.

The last step in the trimerization reaction is the formation of benzene and the corresponding desorption from the active site. The strength of the bond and the adsorption properties of benzene interacting with free and supported Pd atoms are summarized in Table 6. Benzene is more strongly bound to a free isolated Pd atom, 0.76 eV, than to any of the supported atoms where the bonding is of 0.3–0.5 eV except for the case of Pd adsorbed on a F_{3C} defect where the bonding is almost zero. This is a direct consequence of the excess of electron density on supported Pd which facilitates the adsorption and activation of acetylene but increases the Pauli repulsion with benzene once the product is formed. Also the distance of benzene from Pd increases going to the more “basic” MgO sites and shows an anticorrelation with the bond strength, Table 6.

The second interesting aspect is that the energy gain connected to the formation of the aromatic benzene ring from the reaction of adsorbed C₂H₂ and C₄H₄ is smaller for the more “active” sites. Since the bonding of benzene to the various sites shows changes by at most 0.7 eV while the gain in benzene formation differs by up to 2.3 eV, the explanation lies in the different stability of the MgO/Pd(C₂H₂)(C₄H₄) precursor. A relatively high stability of this intermediate in fact will result in a reduced energy release for benzene formation but can also affect the activation barrier for the cyclization process. Transition states and activation barriers have not been considered here, but it is likely that kinetic aspects play an important role in the chemistry of the supported Pd atoms, in particular for reactions where different competing paths are possible.

4. Conclusions

We have performed a computational study of the cyclization of acetylene to benzene on Pd atoms deposited on MgO which is based on reactants and products only, without considering transition states and energy barriers. The study allows one to clarify some of the experimental aspects and to draw some general conclusions about the role of defects on oxide surfaces. The results show that only in the presence of surface defects a single Pd atom becomes an active catalyst for the reaction; in fact, an isolated Pd atom is not capable of adding and activating three acetylene molecules, an essential step for the process. The change in the electronic structure of supported Pd is connected to the electron donor ability of the substrate, which does not simply act as an inert substrate. The oxide surface acts in pretty much the same way as a ligand in coordination chemistry and provides an additional source of electron density, which increases the capability of the Pd atom to back-donate charge to the adsorbed hydrocarbon. In this respect it is remarkable that on transition metal complexes the acetylene trimerization reaction follows a very similar mechanism as on heterogeneous supported catalysts.⁶² The regular oxide anions of the MgO-(001) terraces, however, are not sufficiently active to change the Pd catalytic activity. The basicity of the five-coordinated oxygen atoms in fact is too low, and in any case not sufficient to significantly increase the density on the metal. For the same reason, five-coordinated oxide anions of MgO do not bind CO₂ to form a surface carbonate.⁵² Things are different on low-coordinated oxide anions, such as edge and corner sites. Because of the lower Madelung potential at these sites, the anion basicity is greatly enhanced. More charge is donated to the metal atom, which may become an active catalyst.

The same role is played by another class of surface defects, the neutral oxygen vacancies or F centers. Due to the two electrons trapped in the cavity left by the missing oxygen, these centers are very good basic sites and promote the activity of an adsorbed Pd atom as the low-coordinated oxide anions. Indeed, it has been shown recently that F centers on the surface of polycrystalline MgO are able to reduce very inert molecules such as N₂ leading to metastable N₂[–] radicals.⁶³

The great variety of defect sites at the MgO surface, low-coordinated sites, cation and anion vacancies, divacancies, impurity atoms, etc., makes it difficult to clearly identify the center responsible for the activation of the metal atom. On the other hand, this opens new unexplored possibilities to artificially create specific defects or to control their number and activity, a perspective that leads to the rather new field of defect engineering.

As we mentioned above, an important aspect which has not been investigated here is the role of the support in determining

the activation barriers. In fact, it has been recently observed that small size-selected clusters exhibit specific activity and selectivity when competing reactions are possible.⁶⁴ The different activity and selectivity of catalysts are usually driven by kinetics more than thermodynamic aspects, and it is possible that the various defects change activation barriers as well as thermodynamic stabilities. Work is in progress to partially answer these questions.

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