

Small Pd Clusters, up to the Tetramer At Least, Are Highly Mobile on the MgO(100) Surface

Lijun Xu,¹ Graeme Henkelman,² Charles T. Campbell,¹ and Hannes Jónsson^{1,3,*}

¹*Department of Chemistry 351700, University of Washington, Seattle, Washington 98195-1700, USA*

²*Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712-0165, USA*

³*Faculty of Science, VR-II, University of Iceland, 107 Reykjavík, Iceland*

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Density functional theory calculations predict that small clusters of Pd atoms, containing up to at least four atoms, are highly mobile on the MgO(100) surface with the tetramer having the largest diffusion rate at room temperature—larger than the monomer. Surface vacancies are found, however, to bind the larger clusters strongly enough to trap them. These are important considerations when analyzing the growth and sintering of metal islands on oxide surfaces, in particular, the role of point defects.

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Small metal clusters on oxide surfaces have many interesting properties and potential technological applications, such as in catalysis [1,2], magnetic nanostructures [3], and photonic devices [4]. The size and distribution of the metal clusters strongly influence the functionality of systems. It has, for example, been shown that the efficiency and selectivity of metal-oxide catalysts is a strong function of the size of the metal clusters, making it possible in some cases to tailor catalytic activity by varying the size of the metal clusters [5]. A great deal of effort is now devoted to studies of the properties of small metal clusters on oxide surfaces, in particular, ways of forming and stabilizing islands of the desired size. Some of the key issues are the identification of the diffusion mechanism of the metal atoms, nucleation dynamics, and the role of surface defects. Elegant methods have been developed to deposit size selected clusters softly on the surface so as to prevent breakup [6]. An important issue is the stability of the metal clusters on the surface. Their size tends to increase with time through sintering processes. It is essential to find ways to slow down such processes. In the theoretical study presented here we address this issue by studying the mechanism and rate of diffusion of small metal islands.

The most thoroughly studied metal-oxide system is Pd on MgO(100) [1]. We have, therefore, chosen to carry out our theoretical calculations on this system, but its properties are typical of many other interesting metal-oxide systems [2]. Experimental measurements of Pd islands grown by metal atom deposition at low temperature have shown that the size of the islands is remarkably insensitive to the surface temperature during growth [7]. This is a clear indication that defects play an important role in the growth process. It is well known that oxide surfaces tend to have a high density of point defects (typical estimates being 10^{12} – 10^{13} cm⁻² [8]) in addition to steps and grain boundaries. High-resolution electron-energy-loss spectroscopy (HREELS) spectra have been assigned and interpreted in terms of neutral oxygen vacancies, so called *F* centers, where an oxygen atom has been removed from the surface [9]. It has also been suggested that divacancies are present

where both a Mg and an O atom are missing [8] and, in some cases, charged oxygen vacancies [10].

The traditional view of the growth process is that Pd atoms land primarily on flat MgO terraces and diffuse over the surface by hopping from one site to another. The point defects, however, bind the Pd adatoms so strongly that they get trapped there. A second diffusing Pd adatom which lands on the Pd/defect complex will also get trapped and by the addition of other diffusing adatoms that the Pd cluster builds up at the defect site. Experimental measurements have been analyzed by applying this model and adjusting various energy parameters—such as diffusion activation energy, Pd/defect trapping energy, and dimer binding energy—to fit the measured results. The problem is that different experiments lead to different sets of fitted parameters [1,7]. This suggests that some of the assumptions in the model may not be accurate enough. Theoretical, first-principles calculations have also questioned this model [14]. In particular, the calculated binding energy of a second metal atom to an adatom/*F*-center complex is predicted to be very weak, only 0.39 eV, insignificantly larger than dimer binding energy on the defect free terrace, 0.35 eV [15]. Therefore *F* centers are not predicted to promote dimer formation significantly. In fact, in the case of Pt on MgO, a diffusing adatom would have no energetic preference for binding at an adatom/*F*-center complex and would simply continue to diffuse over the MgO surface [14]. Modeling of Pd/MgO experimental results has required a dimer binding energy at point defects amounting to 1.2 eV in order to fit the measured island size distribution [7]. There is, therefore, significant disagreement between first-principles theoretical calculations and parameters obtained by fitting the standard growth model to experimental results.

We present here theoretical results that indicate a different role for *F* centers in the Pd-island growth process. We have used density functional theory (DFT) to calculate the energy as well as atomic forces and have combined this with the nudged elastic band method [16] and dimer method [17] to identify the mechanism and rate of diffu-

sion, not only of the Pd adatoms but also dimer, trimer, and tetramer islands. The DFT calculations made use of the PW91 functional [18], a plane wave basis set with 270 eV cutoff and ultrasoft pseudopotentials [19] as implemented in the VASP code [20]. A three layer slab of MgO crystal was used to represent the surface, with up to 36 atoms per layer and the top layer free to move. Only the gamma point was included in the k -point sampling. Tests on the Pd adatom confirmed that the change in binding energy was insignificant upon increasing the k -point sampling (-0.02 eV), increasing the plane wave cutoff and using the harder O pseudopotential (0.001 eV), using four layers of MgO instead of three or increasing the vacuum gap or the size of the simulation cell (0.005 eV). We also carried out various other tests (on larger clusters, inclusion of spin polarization, etc.) to verify that these results are converged with respect to computational parameters.

The rate constant for diffusion hops was estimated using harmonic transition state theory [21,22]:

$$k^{\text{hTST}} = \frac{\prod_i^{3N} \nu_i^{\text{init}}}{\prod_i^{3N-1} \nu_i^{\ddagger}} e^{-(E^{\ddagger} - E^{\text{init}})/k_B T}.$$

Here ν_i^{init} and ν_i^{\ddagger} are frequencies of the vibrational normal modes at the initial state and saddle point, respectively. They are determined by displacing the atoms slightly to evaluate the Hessian matrix by finite differences, followed by an evaluation of the eigenvalues and eigenmodes. The results of the DFT calculations for the most stable cluster conformations are summarized in Table I. Remarkably, the tetramer island is found to diffuse fastest at around room temperature, faster than a single Pd adatom. The diffusion mechanism of the various species is discussed in detail below.

A single Pd adatom sits on top of a surface O atom and is bound to the surface by 1.4 eV. It diffuses by hopping over the hollow site in between two O and two Mg atoms [12,13]. The calculated activation energy is 0.34 eV [23]. A typical diffusion hop prefactor of $10^{12}/\text{s}$ is obtained.

TABLE I. Summary of the calculated adsorption energy, $E_{\text{ads}} = E_{\text{Pd}_n/\text{MgO}} - E_{\text{MgO}} - nE_{\text{Pd}(g)}$, diffusion activation energy, $E_d = E_n^{\ddagger} - E_{\text{Pd}_n/\text{MgO}}$, and rate constant prefactor, ν , for diffusion hops of Pd_n clusters with $n = 1-4$. The calculated time in between diffusion hops is given in seconds for a temperature of 200 and 300 K assuming harmonic transition state theory holds. The diffusivity of the tetramer is largest even though the activation energy is slightly higher than for the monomer because the prefactor is anomalously large.

Cluster	E_{ads}/eV	E_d/eV	ν/s^{-1}	τ_D/s	
				200 K	300 K
Monomer	1.4	0.34	7.4×10^{11}	10^{-3}	10^{-6}
Dimer	3.3	0.43	2.5×10^{11}	1	10^{-4}
Trimer	5.7	0.50	1.1×10^{13}	1	10^{-5}
Tetramer	8.8	0.41	1.3×10^{14}	10^{-4}	10^{-7}

This implies the monomer makes diffusion hops a thousand times per second at 200 K and a million times per second at 300 K. The monomer is, therefore, quite mobile on the perfect surface under typical growth conditions. It will, however, tend to get trapped at point defects. The binding energy of a Pd adatom at a F center is 4.0 eV, which is 2.4 eV greater than at the flat MgO terrace [15].

The dimer is found to diffuse primarily through a partial dissociation mechanism (see Fig. 1) in a two step process. The activation energy is only slightly higher than for monomer diffusion, 0.43 eV. The prefactor is rather small and the time between diffusion hops at 200 K is expected to be long, on the order of a second. But, at room temperature the dimer would make 10^4 diffusion hops per second and have surprisingly high mobility. Usually it is assumed that dimers are immobile under typical growth conditions. The dissociation of the dimer into two Pd adatoms is uphill in energy by 0.57 eV at this level of theory (calculations using the B3LYP [24] functional give an even lower value, 0.35 eV [15]) and the process requires overcoming an activation energy barrier of 0.84 eV. Since entropy strongly favors the two monomers over a dimer when the coverage is low, the dimers are rather unstable at elevated temperature.

The trimer has two configurations that are close in energy. The more stable one has two Pd atoms in contact with the substrate, while the third is only bonding to the other two Pd atoms in a bridge position. The less stable configuration has all three Pd atoms in contact with the substrate. This tendency to form strong metal-metal bonds rather than metal-oxide bonds has been noted before in this and other metal-oxide systems [14,25]. The trimer is significantly more stable than the dimer. The breakup into a dimer and monomer adsorbed on the surface is uphill by 1.0 eV. The fastest trimer diffusion mechanism involves

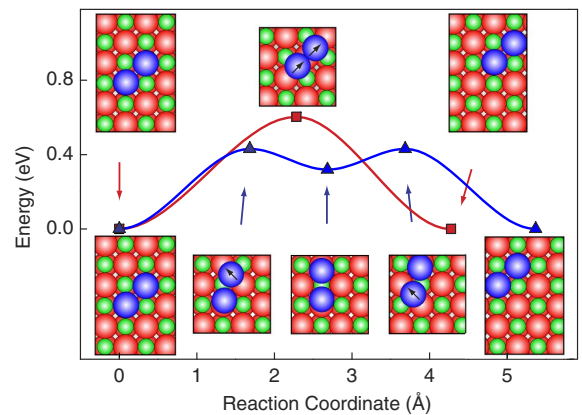


FIG. 1 (color online). Diffusion of Pd dimer on MgO(100). A slide mechanism (red or gray curve) involves a concerted, diagonal displacement of the two atoms. A partial dissociation mechanism (blue or dark gray curve), which has lower activation energy, involves motion of one atom at a time, resulting in an intermediate state with elongated Pd-Pd bond.

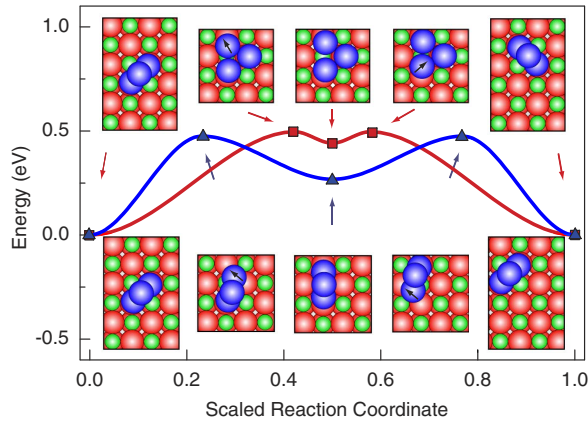


FIG. 2 (color online). Two different trimer diffusion paths with almost the same activation energy: The “walk” (blue or dark gray curve and lower set of insets) and “flip” (red or gray curve and upper set of insets). The rate constant for the latter has a larger prefactor and the diffusion rate is about 100 times faster at room temperature. The total displacement along the minimum energy path for the walk is 7.4 Å and 6.2 Å for the flip.

transitions between these two configurations as shown in Fig. 2. Another mechanism with almost the same activation energy but 10^{-2} smaller prefactor is also shown. At room temperature the trimer diffuses an order of magnitude faster than the dimer.

The tetramer has a slightly distorted trigonal pyramid configuration on the MgO substrate and the ground state is a triplet state [25]. A flat configuration with all four Pd atoms in contact with the oxide is higher in energy by 1.1 eV and the barrier to transform the 2D structure to the 3D pyramid is negligible, on the order of 0.05 eV, as shown in Fig. 3. Even very small Pd islands are, therefore, expected to have a 3D structure. The tetramer is even more stable than the trimer. The breakup into a trimer and a Pd atom adsorbed on the surface are uphill in energy by 1.7 eV.

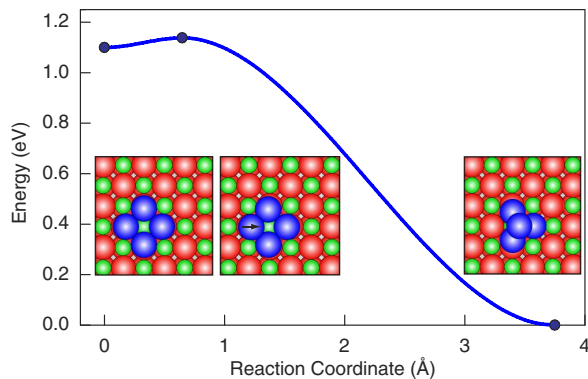


FIG. 3 (color online). Minimum energy path for the formation of a three-dimensional tetramer cluster from a two-dimensional cluster. The activation energy is very small, only 0.05 eV.

The tetramer turns out to have the highest mobility at around room temperature of all the clusters considered here. The diffusion displacements involve a “rolling” movement where the top atom and one of the three base atoms move in a concerted way, as shown in Fig. 4. The prefactor is anomalously large because of two low frequency modes in the transition state. They both resemble frustrated rotation of the Pd atom pair that is not in contact with the oxide. This leads to large vibrational entropy of the transition state and, thereby, a large prefactor in the rate constant, about 10^2 larger than for monomer hopping. At around room temperature, tetramer diffusion is predicted to be faster than diffusion of the monomer by an order of magnitude.

The high mobility of the Pd clusters can have many interesting consequences. Sintering is likely to occur by island coalescence rather than the usual Oswald mechanism where a monomer detaches from a smaller island and attaches to a larger island. These two mechanisms are known to scale differently [26,27]. Furthermore, the mechanism for island formation and the role of point defects may also be different from what is usually assumed. While diffusing Pd adatoms will get trapped at *F* centers, the binding of a second Pd adatom at such a Pd/*F*-center complex to form a Pd dimer is calculated to be small, only 0.39 eV [15]. This slight energetic preference for dimerization is not sufficient to overcome the large entropic preference for two monomers at elevated temperature. The coverage is therefore likely to increase until the more stable trimer or tetramer clusters have formed. Those are highly mobile on the perfect terrace, as discussed above, but get trapped when they encounter a Pd/*F*-center complex. The formation of a tetramer at a *F* center by the merging of a trimer and a Pd/*F*-center

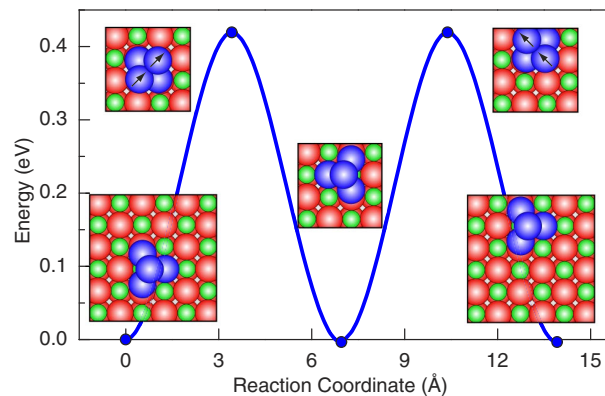


FIG. 4 (color online). Tetramer diffusion mechanism. The top atom and one of the base atoms move in a concerted way as shown in the inset. This rolling mechanism is surprisingly efficient with an activation energy that is lower than for trimer diffusion and a prefactor that is anomalously large mainly because of two soft vibrational modes in the transition state. The tetramer is predicted to diffuse faster than a monomer at room temperature.

complex is calculated to be downhill in energy by 1.2 eV and the analogous formation energy of a pentamer at a F center is 0.8 eV.

The picture that emerges of the growth dynamics at elevated temperature is, therefore, as follows. The first Pd atoms that get deposited on the surface diffuse around until they get stuck at F centers. Additional Pd adatoms are not particularly attracted to the Pd/ F -center complexes but continue to diffuse around the terrace until Pd adatom cluster nuclei of critical size are formed. Clusters formed on the terraces are mobile (at least up to and including the tetramer) and diffuse until they encounter a Pd/ F -center complex. There, the Pd clusters grow in size by one atom if they encounter a Pd/ F -center complex or they merge with a Pd cluster that has already become stuck there. This growth mechanism is more complex than the one typically invoked in the analysis of experimental data on metal overlayer growth. It remains to be seen how well the predicted energetics agree with experimental measurements—this will be the topic of subsequent studies where long time scale simulations will be carried out. The results reported here already indicate that the growth process is more complex than has previously been assumed.

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*Electronic address: hj@hi.is

- [1] C. R. Henry, Surf. Sci. Rep. **31**, 231 (1998).
- [2] C. T. Campbell, Surf. Sci. Rep. **27**, 1 (1997).
- [3] M. Moseler, H. Häkkinen, and U. Landmann, Phys. Rev. Lett. **89**, 176103 (2002).
- [4] T. H. Lee and R. M. Dickson, Proc. Natl. Acad. Sci. U.S.A. **100**, 3043 (2003).
- [5] M. Valden, X. Lai, and D. W. Goodman, Science **281**, 1647 (1998).
- [6] S. Abbet, K. Judai, L. Klinger, and U. Heiz, Pure Appl. Chem. **74**, 1527 (2002).
- [7] G. Haas *et al.*, Phys. Rev. B **61**, 11 105 (2000).
- [8] C. Barth and C. R. Henry, Phys. Rev. Lett. **91**, 196102 (2003).
- [9] M.-C. Wu, C. M. Truong, and D. W. Goodman, Phys. Rev. B **46**, 12 688 (1992).
- [10] Thin MgO films grown on metals, a model system used in laboratory studies of catalyst support, may also have charged vacancies, F^+ centers [11]. But no experimental evidence of such defects has been presented so far. The HREELS spectra show peaks that can be assigned to F centers based on comparison with bulk MgO, although the presence of F^+ centers cannot be ruled out [9]. Vibrational spectra of CO molecules adsorbed on Pd atoms on the MgO surface show redshifted peaks as compared with Pd-CO in the gas phase [12], while theoretical calculations predict a blueshift when the Pd atom is sitting at a F^+ site [13]. The primary point defect, therefore, seems to be the F center, even on the surface of such thin film model systems.
- [11] P. V. Susko, A. L. Shluger, and C. R. A. Catlow, Surf. Sci. **450**, 153 (2000).
- [12] K. Judai *et al.*, J. Phys. Chem. B **107**, 9377 (2003).
- [13] L. Giordano, A. Del Vito, G. Pacchioni, and A. M. Ferrari, Surf. Sci. **540**, 63 (2003).
- [14] A. Bogicevic and D. R. Jennison, Surf. Sci. **515**, L481 (2002).
- [15] L. Giordano, C. Di Valentin, J. Goniakowski, and G. Pacchioni, Phys. Rev. Lett. **92**, 096105 (2004).
- [16] G. Henkelman, B. Uberuaga, and H. Jónsson, J. Chem. Phys. **113**, 9901 (2000); G. Henkelman and H. Jónsson, J. Chem. Phys. **113**, 9978 (2000).
- [17] G. Henkelman and H. Jónsson, J. Chem. Phys. **115**, 9657 (2001).
- [18] J. P. Perdew, in *Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
- [19] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990); G. Kresse and J. Hafner, J. Phys. Condens. Matter **6**, 8245 (1994).
- [20] G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993); **49**, 14 251 (1994); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11 169 (1996).
- [21] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).
- [22] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).
- [23] Calculations using the B3LYP functional [24], which are likely more accurate, have given a slightly higher estimate, 0.41 eV [12,13].
- [24] A. D. Becke, Phys. Rev. A **38**, 3098 (1988); C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
- [25] L. Giordano and G. Pacchioni, Surf. Sci. **575**, 197 (2005).
- [26] D. S. Sholl and R. T. Skodje, Phys. Rev. Lett. **75**, 3158 (1995); Physica (Amsterdam) **231A**, 631 (1996).
- [27] S. D. Liu, L. Bonig, and H. Metiu, Surf. Sci. **392**, L56 (1997).