Zinc Coverage Dependent Structure of PdZn Surface Alloy

Xiang He Yucheng Huang Zhao-Xu Chen*

Supplementary Material

*zxchen@nju.edu.cn

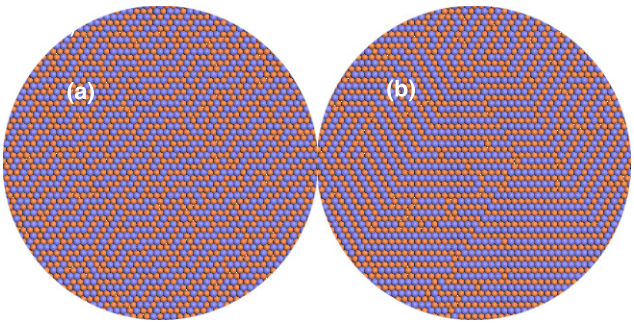

Figure S1: The simulated PdZn alloy pattern of the adlayer of (a) 2 ML Zn coverage and (b) 3 ML Zn coverage at 300 K. The light blue and orange balls denote the Pd and Zn atoms respectively.

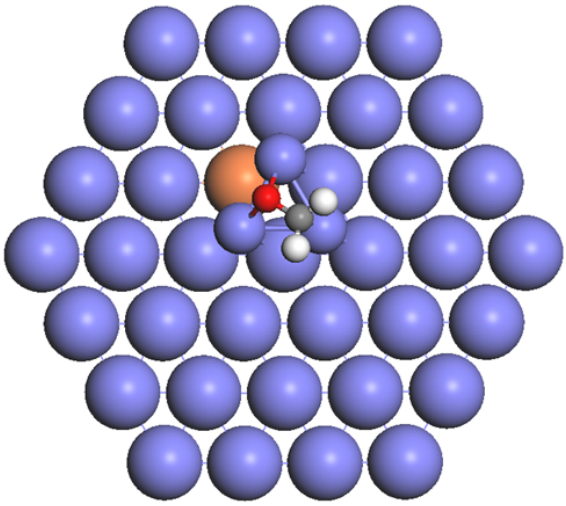

Figure S2: The stable adsorption geometry of formaldehyde at the Pd_3 ensemble on the Pd(111) surface. The substrate is modeled by four layer slab of 4×4 surface unit cell. For brevity only the top layer, Pd_3 island and formaldehyde are displayed. The light blue and orange balls denote the Pd and Zn atoms respectively.

Simulation Method

The Pd(111) substrate is modeled by a rigid three-dimensional slab of 4 layers with 100×100 sites in each layer. Periodic boundary conditions are adopted at XY plane to eliminate the limitation of the cell size. Each site is either unoccupied (vacancy) or occupied by Pd or Zn atom. The occupied site only interacts with the nearest site. Hence there are five pairs of interaction, namely $J_{pp}, J_{zz}, J_{pz}, J_{pv}$ and J_{zv} where the subscript

p, z and v denote Pd, Zn and vacancy respectively. All these parameters are either from first-principles calculations or references.

The formation of surface alloy is simulated by the conventional Monte Carlo method. One atom can be exchanged with one of the nearest neighbour atoms or move to one of the nearest vacancies. Theoretically Zn atoms of the adlayer might diffuse deeply into the Pd substrate by successive exchanging. Experimentally upon evaporating Zn onto Pd(111) substrate, 1:1 multilayer PdZn alloy are formed,[1–3] indicating that formation of surface alloy is more favourable both thermodynamically and dynamically than the diffusion process of zinc atoms into the palladium substrate. Thus we restricted that the exchange depth in the substrate cannot exceed the height of the adlayer.

The exchange attempt is allowed if the transition probability, W, is greater than a randomly generated number between 0 and 1.[4]

$$W = \frac{1}{1 + e^{\Delta E/RT}}$$

where ΔE is the energy difference of the system after the exchange, R is the gas constant and T is the temperature for simulation.

In this paper, a Monte Carlo step is defined when each site that is allowed to be swapped is assigned an exchange attempt. The quantities of interest, such as coverage and island size, are statistically averaged over one million Monte Carlo step after the equilibrium is reached.

The DFT calculations in this paper were performed with VASP[5] package using the projector-augmented wave method[6,7] and the PerdewWang 91 generalized gradient approximation.[8] The substrate is composed of periodic 4×4 unit cells and an energy cutoff of 400 eV was used. For the integration over the Brillouin zone, we combined $5 \times 5 \times 1$ Monkhorst-Pack grids with a generalized Methfessel-Paxton smearing technique to optimize adsorption geometries.

Simulation Parameters

An introduction to determine the pair interactions can be found in Ref. 4. Here the Pd-Pd interaction is evaluated as

$$J_{pp} = -2E_{coh}^{Pd}/12$$

where E_{coh}^{Pd}, 3.70 eV, is the cohesive energy of Pd in the pure metal.[9] The Zn-Zn interaction is evaluated as

$$J_{zz} = 2E_{coh}^{Zn}/12 \cdot \left[\left(\frac{r_{zz}}{r_{pp}} \right)^{12} - 2 \left(\frac{r_{zz}}{r_{pp}} \right)^{6} \right]$$

where E_{coh}^{Zn}, 1.10 eV, is the cohesive energy of Zn in the pure metal.[9] r_{pp} is the nearest distance of Pd-Pd pair in the pure metal. r_{zz} is the nearest Zn-Zn distance in the pure metal. The pair interaction between metal atom and vacancy is evaluated as

$$J_{pv} = (E_V^{Pd} - E_{coh}^{Pd})/12$$

$$J_{zv} = (E_V^{Zn} - E_{coh}^{Zn}) \left(\frac{r_{zz}}{r_{pp}} \right) /12$$

where E_V^{Pd} (1.70 eV) and E_V^{Zn} (0.53 eV) are the formation energies of vacancy in Pd and Zn bulks respectively.[10,11]

To determine the Pd-Zn pair interaction, we designed an exchange process where one Zn adsorbing on the Pd(111) surface exchanges with a surface Pd atom. The exchange energy is formulated as

$$\Delta E = 7(J_{pz} - J_{pp}) + 7(J_{pv} - J_{zv})$$

The above exchange energy (ΔE) is calculated to be 0.118 eV by DFT methods. Thus the Pd-Zn pair interaction is -0.479 eV. Hence all the five pair interactions have been figured out, which are summarized in Table S1.

Table S1: Pair interactions in eV

	Pd	Zn	Vacancy
Pd	-0.617	-0.479	-0.167
Zn	-	-0.178	-0.046
Vacancy	-	-	

References

[1] W. Stadlmayr, S. Penner, B. Klötzer and N. Memmel, *Surf. Sci.*, 2009, **603**, 251–255.

[2] H. Gabasch, A. Knop-Gericke, R. Schlögl, S. Penner, B. Jenewein, K. Hayek and B. Klötzer, *J. Phys. Chem. B*, 2006, **110**, 11391–11398.

[3] A. Bayer, K. Flechtner, R. Denecke, H. Steinrück, K. M. Neyman and N. Rösch, *Surf. Sci.*, 2006, **600**, 78–94.

[4] D. Chen and Y. Wang, *J. Mater. Sci.*, 2005, **40**, 3461–3466.

[5] (*a*) G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558; (*b*) G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251; (*c*) G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50; (*d*) G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.

[6] P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.

[7] G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.

[8] J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.

[9] Z. Chen, K. M. Neyman, A. B. Gordienko and N. Rösch, *Phys. Rev. B*, 2003, **68**, 075417.

[10] T. R. Mattsson and A. E. Mattsson, *Phys. Rev. B*, 2002, **66**, 214110.

[11] R. Balzer and H. Sigvaldason, *J. Phys. F: Met. Phys.*, 1979, **9**, 171–178.