

Mapping the Shape and Phase of Palladium Nanocatalysts

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1 Supplementary Information

The calculations in this study were performed using Density Functional Theory (DFT) within the Generalized-Gradient Approximation (GGA), with the exchange–correlation functional of Perdew and Wang (PW91)¹. This has been implemented via the Vienna Ab initio Simulation Package (VASP)^{2,3}, which spans reciprocal space with a plane-wave basis expanded to a given kinetic energy cut-off (in this case 325 eV), and utilizes an iterative self-consistent scheme to solve the Kohn-Sham equations using an optimized charge-density mixing routine. All calculations were performed using the Projected Augmented Wave (PAW) potentials^{4,5}, with spin polarization, to an energy convergence of 10^{-4} eV. Using this approach the lattice parameter for bulk Pd was found to be 3.891 Å, which compares well with the experimental value of 3.8907 Å.⁶

The surfaces properties were computed using periodic slabs generated by cleaving a three dimensional (periodic) super-cell along the crystallographic planes of interest, and adding a 15 Å layer of vacuum space. The periodic super-cell each consisted of 2×2 surface-cells, with thicknesses of 4.318 nm for the (111) surfaces (so the slab contained 80 atoms), 4.314 nm for the (110) surfaces (so that the slab contained 128 atoms), and 4.527 nm for the (100) surfaces (so that the slab contained 96 atoms). These are structures used a $6 \times 6 \times 1$, $4 \times 4 \times 1$ and $4 \times 4 \times 1$ reciprocal k-mesh, respectively, and are shown in figure 1. In each of these structures, the surfaces were fully relaxed by optimizing the atoms in the 4 outer most atomic layers (the terminal plane, and three further planes beneath), while the atomic planes in the center of the slabs were restricted to the bulk-like atomic positions (which is consistent with the experimental observations). This has the advantage of providing more surfaces for analysis (both upper and lower facets), will still constraining the bulk like positions far from the surface. The relaxations were performed using an efficient matrix-diagonalization routine based on a sequential band-by-band residual minimization method of single-electron energies^{7,8} with direct inversion in the iterative subspace. This methodology has previously been used successfully to model the surfaces of metals^{9–11}, and for use in modelling the morphology of metal nanostructures.^{12–14}

Based on these simulations the surface energies γ_i (for a surface in orientation $i = hkl$), can be defined in terms of μ_{Pt} , the chemical potential of bulk FCC platinum as follows:

$$\gamma_i(0) = \frac{1}{2A_i} \left[E_i(N) - N\mu_{\text{Pt}} + P\Delta V - T\Delta S \right], \quad (1)$$

where $E_i(N)$ is the total energy of a fully relaxed surface slab in orientation i (containing N platinum atoms), A_i is the explicit area of the supercell in the plane of the surface, P is the pressure, ΔV is the volume change due to surface relaxation, T is the temperature and ΔS is entropy change which is normally dominated by the vibrational entropy from phonons. Since all of the simulations were performed here at low temperature (and extrapolated to $T = 0$ K), the second term is zero. The entropic contributions must be added empirically, as described in the main text, and rigorously validated in reference 12. Furthermore,

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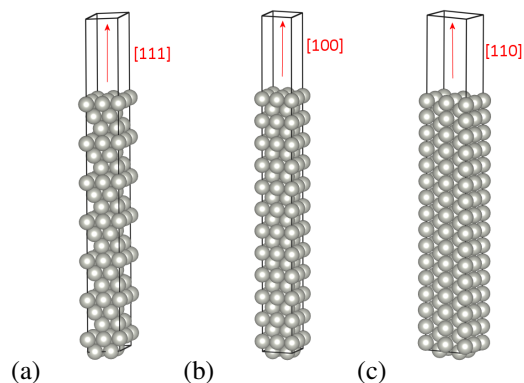


Fig. 1 (a) the (111) surface slab, (b) the (100) surface slab, and (c) the (110) surface slab. The relaxation was restricted to the 4 terminal layers of the upper and lower surfaces, while the central planes were constrained to the bulk-like positions.

although surface reconstructions were observed, the second last term will be disregarded, as inaccuracies introduced by the omission will be less than the uncertainties inherent in the DFT calculations.

Using this technique, the surface energy was calculated for all of the low index surfaces of interest. The isotropic surface stresses were computed from the trace of the surface stress tensor, which is output directly by the VASP code. These results are provided below in Table 1, along with similar results obtained by others, for the purposes of comparison. There are numerical difference between the results obtained by different studies, due usually to different DFT approximation, exchange correlations functional, meshes sizes and convergence criteria, but we see that in cases where authors have treated more than one surface or value, the relative values are (for the most part) consistent among the different sets. Since the intention here is to use these values to determined the shape of nanoparticles enclosed by these surfaces (see Main Text), it is the relative values that are important, and so it is imperative that a consistent set of values is calculated using the same method.

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Table 1 Comparison of surface and elastic properties: surface energies and isotropic stresses are in J/m², and the bulk modulus is given in GPa. * average over all surfaces (including other higher index surfaces not considered here).

Method [Reference]	γ_{111}	γ_{110}	γ_{100}	σ_{111}	σ_{110}	σ_{100}	B ₀
GGA [This Study]	1.160	1.594	1.373	1.443	1.708	1.591	176 ± 1.15
EAM [15]	1.163	1.392	1.293	1.634	1.402	1.685	
EAM [16]	1.22	1.49	1.37				
EAM [17]				1.16	1.14	0.81	
MEAM [18]	1.38	1.65	1.66	3.14	1.42	2.69	
LMTO [19]	1.64	1.97	1.86				
TB [20]	1.69	2.00	1.78				
TB [21]	1.570	1.860	1.75				212
NRL-TB [22]	1.67	2.02	1.85				
KKR-LDA [23]	2.01	2.39	2.22				
FCD-GGA [24]	1.920	2.225	2.326				
GGA [25]	1.314	3.204	1.506				
GGA [26]	1.299	1.540					
Expt. [27]		2.003*					
Expt. [28]		2.050*					
Expt. [6,29]							184

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