

**Supporting information for:**  
**CO-Induced Restructuring on Stepped Pt**  
**Surfaces: A Molecular Dynamics Study**

Joseph R. Michalka,<sup>†,‡</sup> Andrew P. Latham,<sup>†</sup> and J. Daniel Gezelter<sup>\*,†</sup>

*<sup>†</sup>Department of Chemistry and Biochemistry*

*University of Notre Dame*

*251 Nieuwland Science Hall*

*Notre Dame, Indiana 46556*

*<sup>‡</sup>Department of Chemistry and Physics*

*Southwest Baptist University*

*Wheeler Science Facility*

*Bolivar, Missouri 65613*

E-mail: [gezelter@nd.edu](mailto:gezelter@nd.edu)

Phone: (574) 631-7595

Step-wandering during the simulations can interfere with easy interpretation of the generalized coordination figures. Figure S1 provides an additional ideal surface to complement the ideal Pt(321) GCN distribution shown in the main paper. The Pt(557) surface has straight step edges, and the GCN distribution therefore has fewer peaks than the Pt(321) surface.

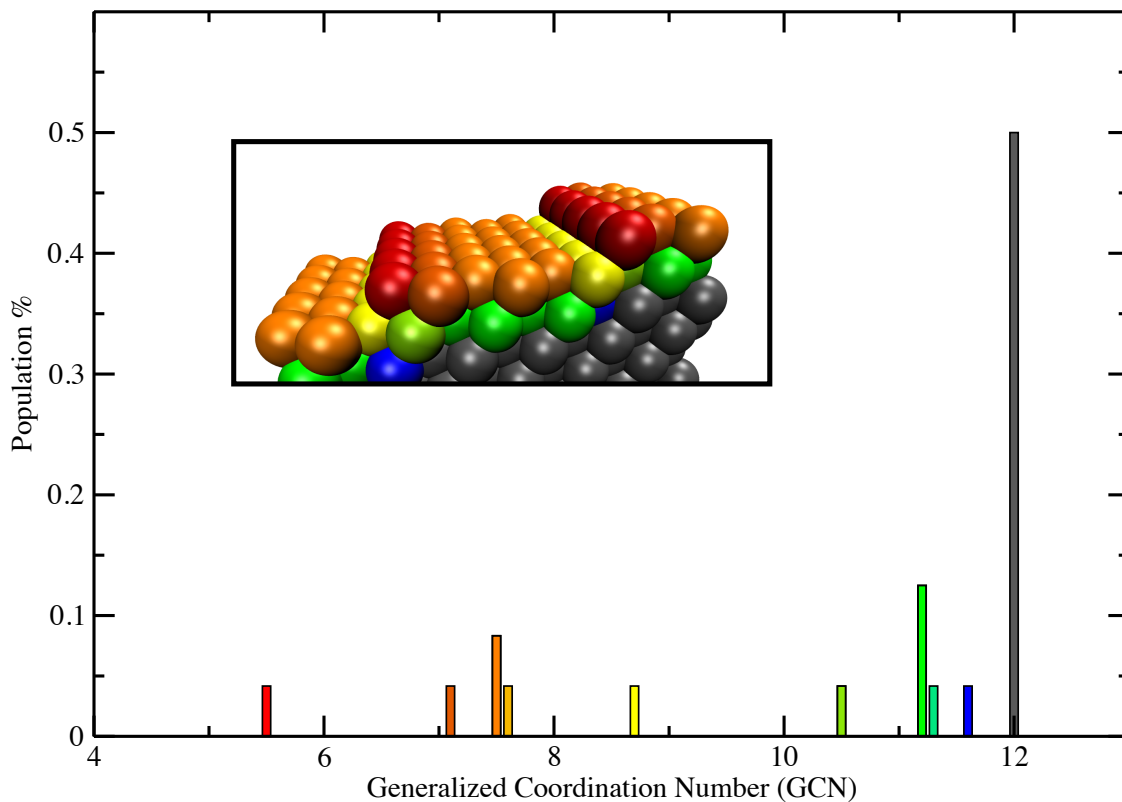


Figure S1: The generalized coordination number of an ideal Pt(557) system colored to match the inset structure. Other than the bulk (GCN = 12), the ideal (557) surface displays a variety of coordination environments at its surface. The under-coordinated edge atoms (red) have the lowest GCN, where the plateau atoms have GCN values around the ideal (111) surface number of 7.5. Subsurface atoms (yellow, greens, and blues) have a larger GCN than the surface, but are still less coordinated than the bulk.

The Pt(557) surface did not exhibit step doubling in the simulations reported in this work, so the distribution of generalized coordination numbers did not undergo significant changes, as shown in Figure S2.

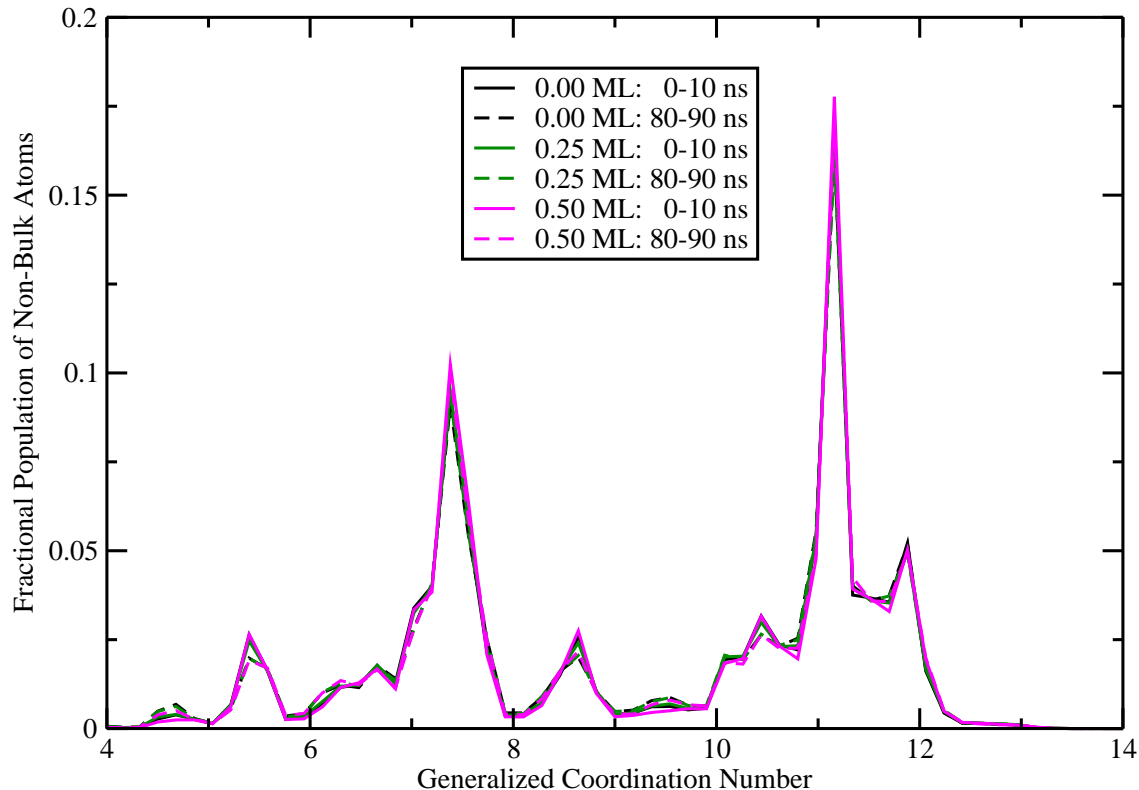


Figure S2: The distribution of generalized coordination numbers (GCN) for the near-surface atoms of the Pt(557) LS systems. Solid lines represent the averaged GCN during the first 10 ns of simulation time, while dotted lines correspond to the last 10 ns. Black, green and magenta lines depict the 0, 0.25, and 0.5 ML systems respectively. Except for a small decrease at GCN values of 5.5 and 10.5, minimal changes were observed.

On the Pt(765) surfaces, reconstruction on only the MS 0.5 ML system was observed, but none of the other surfaces exhibited reconstruction beyond step wandering. The slight increase in the peak at GCN  $\sim 7.5$  suggests that this measurement is sensitive to relatively minor surface reconstruction, like the step-edge doubling and disappearance highlighted in Figure S6.

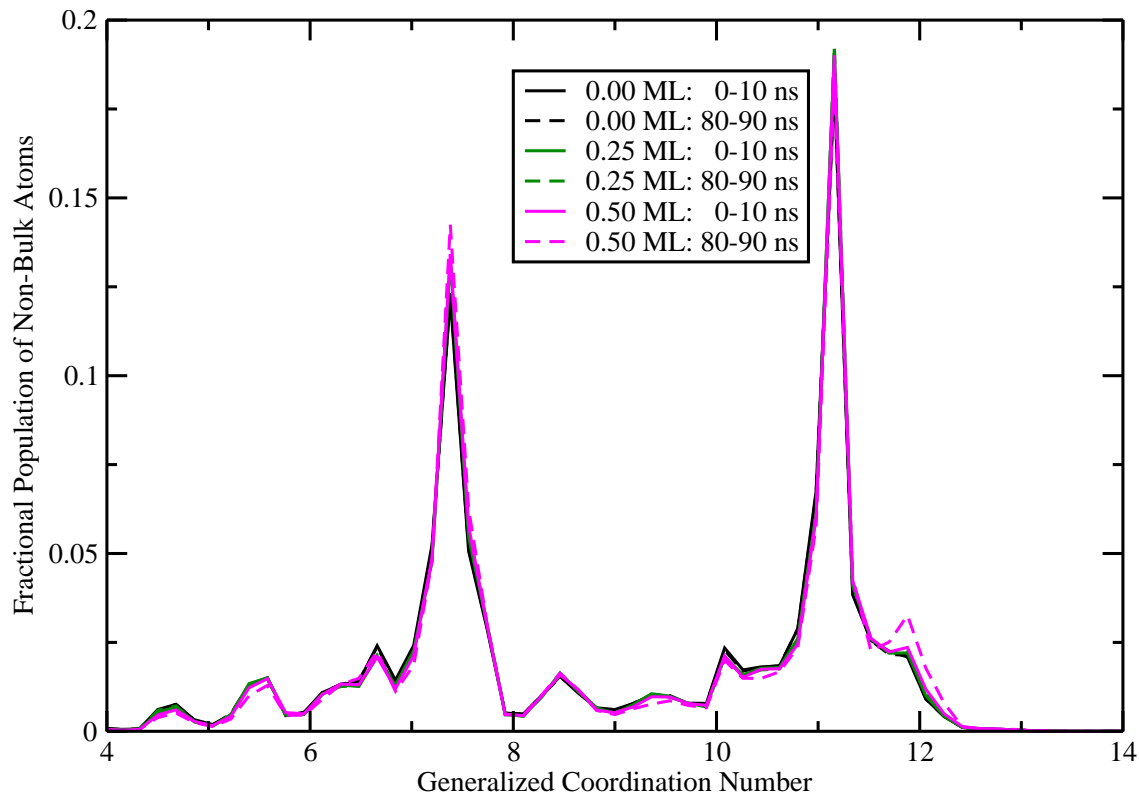


Figure S3: The distribution of generalized coordination numbers (GCN) for the near-surface atoms of the Pt(765) MS systems. Line styles and colors are the same as in Fig. S2. The increasing peak heights seen at GCN  $\sim 7.5$  and  $11.8$  capture the doubling process explored in Figure S6.



The increase in the peak height at  $\text{GCN} \sim 6.8$  for the 0 and 0.5 ML LS systems appears to be capturing the loss of the clean (765) surface. In contrast, the 0.25 ML LS system only exhibited step-edge wandering, but generally maintained the originally-displayed edges.

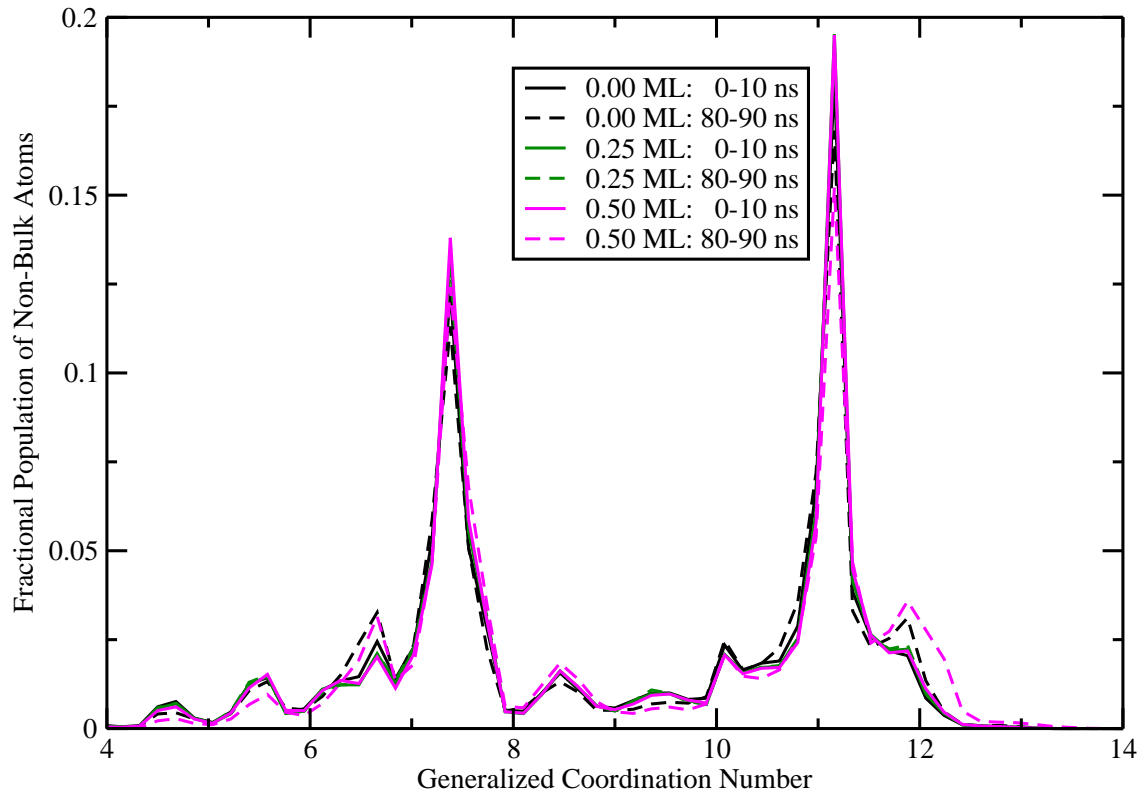


Figure S4: The distribution of generalized coordination numbers (GCN) for the near-surface atoms of the Pt(765) LS systems. Line styles and colors are the same as in Fig. S2. The increasing peak heights seen at  $\text{GCN} \sim 6.8$  and  $11.8$  for the 0.0 and 0.5 ML systems capture the disruption mentioned in the main text.

The Pt(112) systems explored in this study were run at temperatures close to a surface melting transition. One reflection of this is the partial sinking of step edges into the surface. In Figure S5, a few of the edges maintained  $\{100\}$  step facets and were a source for adatoms. However, the sunken steps rarely ejected adatoms, and for the majority of the simulation, exhibited minimal movement on the surface.

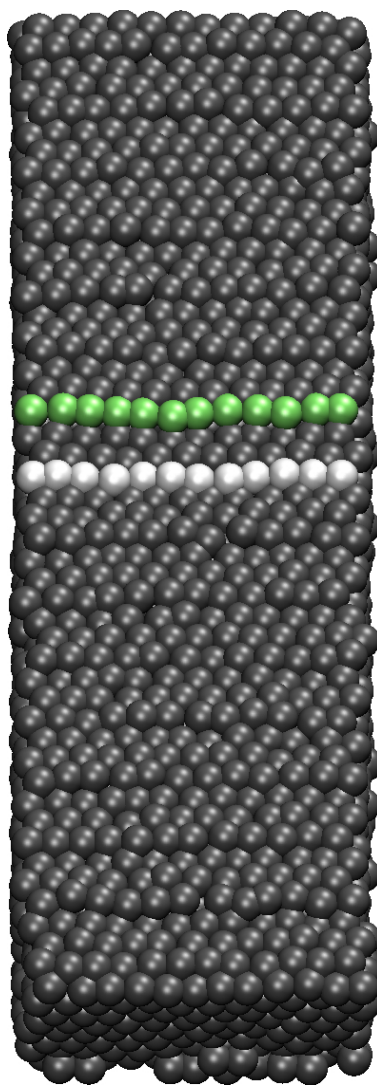


Figure S5: The Pt(112) systems have a large surface energy, and exhibited restructuring that resulted in many of the  $\{100\}$  steps sinking into the surface (white) and shifting half a unit-cell to display a sunken  $\{111\}$  step edge. A few step edges (green) retained  $\{100\}$  step edge morphology and were the primary source for adatom formation and edge wandering.

The kinked edges and large plateaus of the Pt(765) systems help distinguish which surface attributes were most important in encouraging or hindering surface reconstruction. No clear step-doubling occurred on these surfaces despite a significant amount of step-wandering. On the 0.5 ML MS system shown in Fig. S6, what were originally two separate steps, coalesced into a single step located at an intermediate distance between the original step edges. A portion of each step sunk into the surface allowing the two remaining plateaus to meet up to form a single step edge.

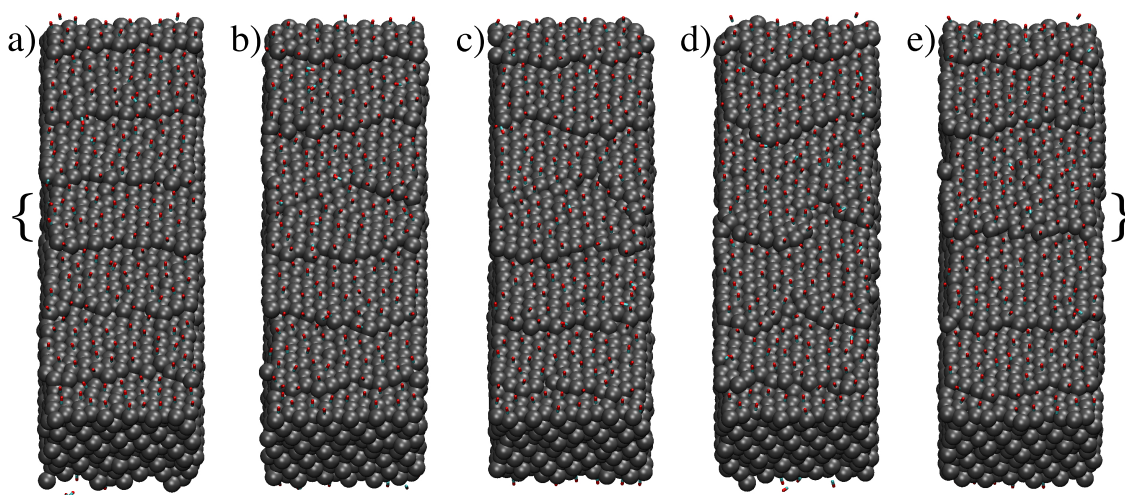


Figure S6: The Pt(765)-MS 0.5 ML system (a) 0 ns, (b) 33.4 ns, (c) 50.2 ns, (d) 75.1 ns, (e) and 100 ns after exposure to CO. The step-edges indicated with a bracket in (a) approach each other while sinking into the surface. The result is a step-edge that is between the starting points of both parents, but which is only one atom elevated from the surface.