

Reactive 1D gold oxide chains on nanoporous gold

Studying the Wet and Dry CO Oxidation on Nanoporous Gold Using Static DFT Computations and AIMD Simulations

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In Short

- We demonstrate the self-organization of adsorbed oxygen atoms into $-(\text{Au-O})-$ chains on stepped gold surfaces and investigate the influence of co-adsorbates on this process.
- The formation of $-(\text{Au-O})-$ chains and dynamic surface restructuring are potentially crucial for the catalytic performance and selectivity of nanoporous gold.
- Utilizing *ab initio* molecular dynamics, we explore the dynamic mechanisms underlying surface restructuring, the displacement of adsorbates on the surface, and various reactions on nanoporous gold.

Nanoporous gold (np-Au) consists of a porous three-dimensional gold nanostructure, with pore sizes ranging from a few nanometers to several hundred nanometers.^{1,2} It finds applications in various fields including catalysis, sensing, and optical applications. Np-Au is produced through dealloying, where a less noble metal (such as silver) is selectively removed from a gold alloy. This material has demonstrated exceptional catalytic properties due to its high activity and selectivity. However, the complex surface chemistry of np-Au poses challenges for study and modeling. As a result, simpler gold systems, such as well-defined stepped Au surfaces, are often used as models.³

Previous studies on Au surfaces typically relied on an idealized reaction models that assumed (i) no surface restructuring during the reaction, (ii) a clean surface with no other adsorbed species apart from the reactants, and (iii) no parallel reactions or diffusion processes. In our project, we have adopted a more unbiased approach by pseudo-randomly placing adsorbates on our gold surface using a custom Python script. We then optimize the structure and use *ab initio* molecular dynamics to observe how temperature and adsorbates affect the surface over time. We utilize Au(221) as the gold surface in this study, due to its similar surface properties to Au(332), which is used experimentally by our collaborators. Our adsorbates include carbon monoxide (CO), atomic or molecular oxygen (O or

O_2), and water. The adsorption and oxidation of CO are prototypical reactions in heterogeneous catalysis. Np-Au catalysts, with their intricate structures, trace impurities of less noble metals, and adsorbed atomic oxygen, can undergo surface restructuring during CO oxidation.⁵

During catalysis, adsorbates cover the np-Au surface, causing restructuring and impacting catalytic performance over time. This project investigates how various adsorbates influence surface restructuring and how dynamic surface evolution can be driven by catalytic reactions. We also investigate how the presence of additional adsorbates affects the formation of $-(\text{Au-O})-$ straight chains on Au(221), as well as the reactions occurring between O and H_2O , O and CO, CO and O_2 and CH_3OH and O_2 adsorbates. Continuing from previous work, we have found that oxygen atoms adsorbed near the Au(221) step edge tend to self-organize into quasi-ordered Au-O-Au-O chains, accompanied by significant surface restructuring. See Figure 1. Overall, we have found that where the O atoms are placed on the surface, affects the amount of surface restructuring and O atom displacement possible.^{6,7}

In our past project period, we have shown that the presence of CO molecules alongside O atoms on Au(221) slows down the formation of $-(\text{Au-O})-$ straight chains as well as the amount of surface restructuring and oxygen atom mobility, while $\text{CO} + \text{O} \rightarrow \text{CO}_2$ reactions occur at the step edges. These reactions involved AuCO complexes, however when considering the activation barriers of $\text{CO} + \text{O} \rightarrow \text{CO}_2$ and $\text{AuCO} + \text{O} \rightarrow \text{CO}_2 + \text{Au}$, we found no significant difference, and in both cases the barriers were low (< 0.07 eV).

We showed in our past and current project periods that CO and O_2 adsorbed on AuAg(221) with or without randomized Ag atoms, results in $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$ reactions occurring via the associative mechanism, as discussed in 4, however in these systems very little surface restructuring occurs. See Figure 2 for snapshots of one of these simulations. We are using the same structure in another simulation as in Figure 2 but with CO replaced by CH_3OH , however this run is still at its early stages.

We have also considered in this current project period water molecules co-adsorbed alongside atomic

O on Au(221). This simulation is still incomplete, but we have noticed the formation of OH and OH₃ groups, alongside high water mobility, minor surface restructuring and some -(Au-O)- chain formation. Comparing to the same setup just without water, it appears thus far that the presence of water does hinder chain formation and has a small effect on the amount of surface restructuring, by lowering it. See Figure 3 for snapshots of this run.

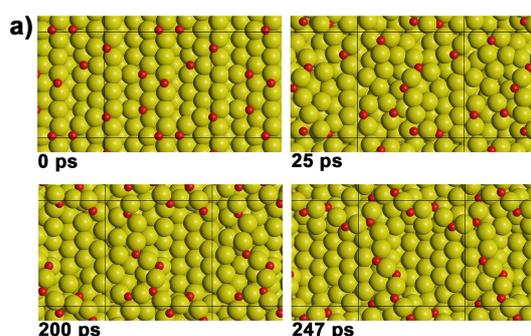


Figure 1: Snapshots of the AIMD simulation involving multiple randomly placed oxygen atoms on the Au(221) surface. The unit cells have been multiplied/repeated for better visualization. Red balls = oxygen; Yellow balls = gold atoms.

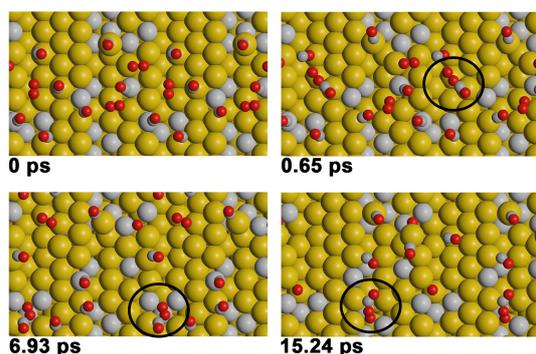


Figure 2: Snapshots of the AIMD simulation involving CO molecules and O₂ molecules on the Au(221) surface. The unit cells have been multiplied/repeated for better visualization. Large silver balls = silver atoms; small grey balls = carbon; Red balls = oxygen; White balls = gold atoms initially at step edge; Yellow balls = gold atoms; Pink balls = Au adatom.

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More Information

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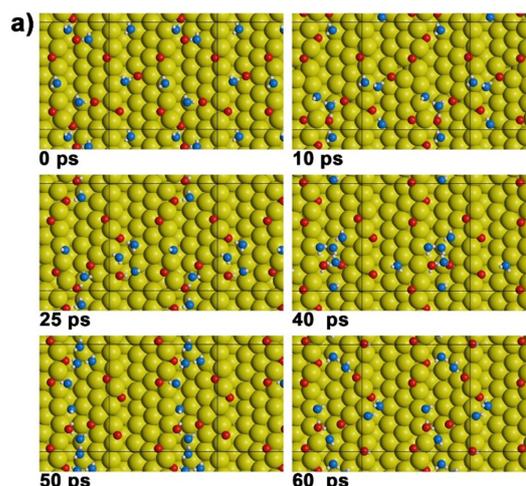


Figure 3: Snapshots of the AIMD simulation involving H₂O molecules placed randomly on the Au(221) surface, alongside O atoms. The unit cells have been multiplied/repeated for better visualization. Yellow balls = Au; Red balls = oxygen; White balls = H; Blue balls = O (water).

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