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

L. Moskaleva, S. Li, Institut für Angewandte und Physikalische Chemie, Universität Bremen

In Short

- We show how adsorbed oxygen atoms self-organize on stepped Au surfaces to form -(Au-O)-chains and how co-adsorbates affect this process

- Dynamic surface restructuring and -(Au-O)- chain formation may be important for the catalytic activity and selectivity of nanoporous gold

- Using *ab initio* molecular dynamics, we can investigate the dynamic mechanistic picture of surface restructuring (on nanoporous gold), self-organization of oxygen atoms and a variety of reactions

Nanoporous gold (np-Au) is a porous three-dimensional nanostructure of gold, with pore sizes ranging from a few nanometers to a few hundreds of nanometers. It has many applications in a variety of fields such as catalysis, sensing, optical applications, etc. [1,2] Np-Au is prepared by dealloying, a process in which a less noble metal (such as silver) is selectively leached out from a gold alloy. Over the years, np-Au has been shown to have remarkable catalytic properties, due to its high activity and selectivity. However, np-Au has a complex surface chemistry, which makes it difficult to study and model. Therefore, simpler gold systems are used to represent or model it, such as well defined stepped Au surfaces. Most previous studies of CO reactivity on Au surfaces assumed an idealized reaction model, where (i) the surface did not restructure during the reaction, (ii) the surface was clean, i.e. no other adsorbed species apart from the reactants, and (iii) no parallel reactions or diffusion processes were considered. In our project, we use a more unbiased approach by pseudo-randomly placing adsorbates on our gold surface using an in-house python script. Then we optimize the structure and apply *ab initio* molecular dynamics to measure how temperature and adsorbates can affect the surface over time. We use Au(221) as the gold surface in this project, as it shares similar surface properties to Au(332) used experimentally by our project partners. The adsorbates we use are carbon monoxide (CO) and atomic or molecular oxygen (O or O_2) as well as water. Adsorption and oxidation of CO is a common prototypical reaction in heterogeneous catalysis. Np-Au catalysts have complex structures (with trace impurities of less noble metals, adsorbed atomic O and possibly other adsorbates on its surface), and may undergo surface restructuring upon CO oxidation.

During catalysis, the surface of the np-Au catalyst is covered by adsorbates causing the surface to restructure and affecting its catalytic performance. Therefore, in this project we investigate how various adsorbates, potentially affect the surface restructuring, and how a dynamic surface evolution can be driven by a catalytic reaction. This project continues previous work from our group, in which we have found that oxygen atoms adsorbed close to the Au(321) step edge tended to self-organize into quasi-ordered Au-O-Au-O chains, with some surface restructuring taking place.[3] Our group has also shown that oxygen atoms adsorbed as an infinite Au-O chain at the Au(221) step edge, have a more favorable adsorption energy than oxygen atoms in any other location.[4]

In this project we studied O atoms that are randomly dispersed across the Au(221) surface, and analyzed the resulting surface restructuring. As shown in Figure 1, O atoms adsorbed on Au(221) can have a pronounced effect on its surface restructuring, with the oxygen atoms self-organizing to form a long Au-O chain. However, if the O atoms already start off in a long chain, little surface restructuring is evident. This part of the work also highlighted that surface Au mobility increases due to the O atoms pulling the Au atoms across the surface. This is supported by an experimental transmission electron microscopy study.[5] Similarly, in Figure 2, we considered CO molecules adsorbed on the Au(221) surface, with noticeable surface displacement occurring, especially around the step Au atoms. The CO molecules also end up sitting close or on top of the step Au atoms, while some form AuCO complexes.

For mixtures of adsorbed CO and O, we have observed that the CO molecules slow down the formation of -(Au-O)- chains, with less surface restructuring occurring than expected. Furthermore, all CO_2 formation reactions occur via O-Au-CO complexes reacting with O atoms or CO molecules. When considering an AuAg(221) surface with CO and O_2 molecules adsorbed on the surface, we have observed these molecules reacting via an associative mechanism to form CO_2. That is, the two molecules first form an OCOO intermediate,
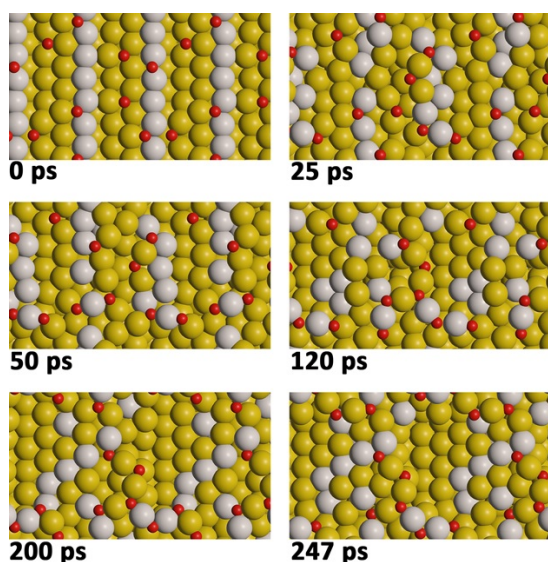
Figure 1: *Snapshots of the AIMD simulation involving multiple randomly placed oxygen atoms on the Au(221) surface. The unit cells have been multiplied/repeated for better visualization. Red balls = oxygen; White balls = gold atoms initially at step edge; Yellow balls = gold atoms.*

Figure 2: *Snapshots of the AIMD simulation involving CO molecules placed randomly on the Au(221) surface. The unit cells have been multiplied/repeated for better visualization. Grey balls = carbon; Red balls = oxygen; White balls = gold atoms initially at step edge; Yellow balls = gold atoms.*

which then decomposes into CO_2 and O. This agrees with our recent study,[4] where we used static DFT computations and NEB calculations to show that the associative mechanism is the preferred mechanism on Au(221).

In the final project phase we plan to investigate the effect of Ag atoms distribution, the role of co-adsorbed water and the O-Au-CO complex in the reactions. We also want to look at other catalytically relevant metals, such as Pt and Ag, and apply predictive molecular dynamics to improve our simulations.
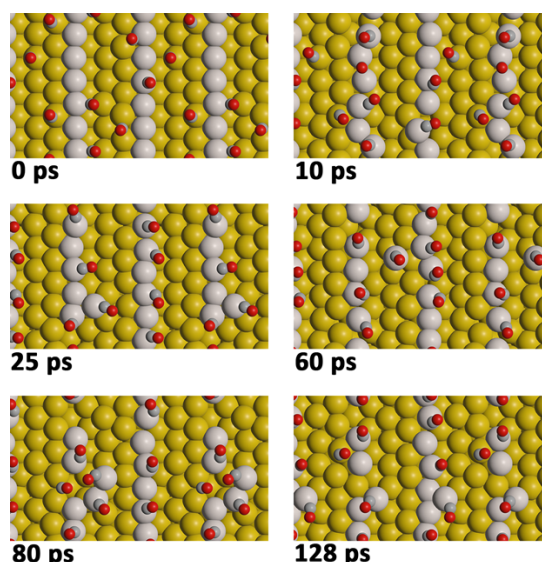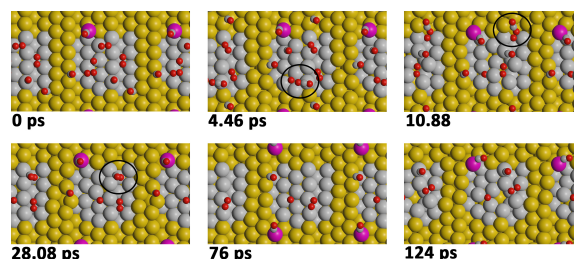

Figure 3: *Snapshots of the AIMD simulation involving CO molecules and O_2 molecules on the Au(221) surface. The unit cells have been multiplied/repeated for better visualization. Large silver balls = silver atoms; small grey balls = carbon; Red balls = oxygen; White balls = gold atoms initially at step edge; Yellow balls = gold atoms; Pink balls = Au adatom.*

More Information

[1] G. Wittstock, M. Bäumer, W. Dononelli, T. Klüner, L. Lührs, C. Mahr, L. V. Moskaleva, M. Oezaslan, T. Risse, A. Rosenauer, A. Staubitz, J. Weissmüller, A. Wittstock, Chem. Rev. 123, 6716-6792 (2023)

[2] A. Wittstock, J. Biener, M. Bäumer, Phys. Chem. Chem. Phys., 12, 12919-12930 (2010)

[3] Y. Li, W. Dononelli, R. Moreira, T. Risse, M. Bäumer, T. Klüner, L. Moskaleva, J. Phys. Chem. C, 122, 5349-5357 (2018)

[4] S. Li, O. Olaniyan, L. Carroll, M. Baümer, L. Moskaleva, Phys. Chem. Chem. Phys. 24, 28853-28863 (2022)

[5] T. Fujita, T. Tokunaga, L. Zhang, D. Li, L. Chen, S. Arai, Y. Yamamoto, A. Hirata, N. Tanaka, Y. Ding, M. Chen, Nano Lett. 14, 1172-1177 (2014)

Funding

DFG Subject Area

302-03