



Contribution ID: 63

Type: Student Micro-talk

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

Investigating the adsorption behavior and reactivity of catalytically relevant molecules on well-defined gold surfaces provides great information for understanding the catalytic activity of gold-based nanocatalysts, such as nanoporous gold (np-Au). Within this project we aim to deliver a comprehensive picture of surface reactivity, where an idealized picture of a perfect clean and rigid catalyst surface will be replaced by a surface, which is covered by adsorbates and is dynamically changing during catalytic transformations. These insights will be achieved through a combination between traditional (static) calculations based on density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations. The work of DFG Research Unit NAGOCAT already revealed that the surface chemistry of np-Au turns out to be more complex than anticipated. Interactions between gold, chemisorbed O atoms generated and consumed during catalysis, and trace amounts of Ag impurities present in np-Au lead to complex surface dynamics. To shed more light into these surface evolution processes, we will study the surface reactivity by means of AIMD simulations. Adsorption and oxidation of carbon monoxide (CO) is a common prototypical reaction in heterogeneous catalysis. Nanoporous gold catalysts have complex structures (with trace impurities of less noble metals), and may undergo surface restructuring upon CO oxidation. In fact, atomic O on its own can lead to rapid restructuring with metal diffusion happening at the same time. In a recent DFT study, it was found that oxygen atoms tend to self-organize on stepped Au surfaces and thus might not prefer to adsorb individually. In particular, in the presence of oxygen, admetal Ag segregates and quasi ordered Au-O-Au-O chains are likely to form.

Our previous AIMD study of CO oxidation with O₂ on the inverse ceria/Au catalyst helped us to identify a Mars-van-Krevelen (MvK) type of mechanism, where lattice O of a ceria particle at the Au/oxide interface was participating in the catalytic cycle [2]. In this project we hypothesize that O atoms in 1D Au oxide structures might behave similarly to ceria on Au, providing storage for active O atoms and releasing them in MvK-type redox processes. Additionally, we expect that the CO oxidation could lead to an even faster formation of O phases and surface restructuring, as well as admetal segregation.

The project will focus primarily on the mechanism and dynamic restructuring of model Au catalysts with 1D gold oxide structures supported on Au during dry and wet CO oxidation using AIMD. AIMD simulations allow one to study (the mechanism of) a chemical reaction and surface processes (such as surface and subsurface metal diffusion) together over the same time scale, something that conventional static DFT computations do not offer. This will help us get a new level of understanding of the CO oxidation of np-Au that could be extended to more complex probe molecules.

Static DFT computations will be coupled with AIMD simulations as to explore potentially interesting/relevant AIMD reaction pathways, specifically since AIMD simulations only help to identify a pathway, but afterwards static calculations are required to calculate stationary points and determine activation barriers along the pathway.

References:

- [1] Y. Li, W. Dononelli, R. Moreira, T. Risse, M. Baumer, T. Kluner, L. V. Moskaleva; Oxygen-driven surface evolution of nanoporous gold: Insights from ab initio molecular dynamics and Auger spectroscopy, *J. Phys. Chem. C* 22 (2017) 5349-5357.
- [2] Y. Li, S. Li, M. Baumer, E. A. Ivanova-Shor, L. V. Moskaleva; What Changes on the Inverse Catalyst? Insights from CO Oxidation on Au-Supported Ceria Nanoparticles Using Ab Initio Molecular Dynamics, *ACS Catal.* 10 (2020) 3164-3174.

Student?

Yes

Supervisor name

Professor Lyudmila Moskaleva

Supervisor email

lyudmila.moskaleva@gmail.com

Primary author: CARROLL, Lenard (University of the Free State)

Presenter: CARROLL, Lenard (University of the Free State)

Session Classification: Micro-talks

Track Classification: Computational Chemistry