The role of oxides for CO oxidation over Pd and Rh, and how to deal with oxygen poisoning

Johan Gustafson[1], Olivier Balmes[2], Chu Zhang[1], Mikhail Shipilin[1], Andreas Schaefer[3], Benjamin Hagman[1], Lindsay R. Merte[2], Natalia M. Martin[3], Per-Anders Carlsson[3], Maciej Jankowski[4], Ethan J. Crumlin[5], and Edvin Lundgren[1]

[1]*Synchrotron Radiation Research, Lund University, SE-221 00 Lund, Sweden*
[1]*MAX IV Laboratory, Lund University, SE-221 00 Lund, Sweden*
[3]*Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden*
[4]*European Synchrotron Radiation Facility, CS40220, 38043 Grenoble Cedex 9, France*
[5]*Advanced Light Source, Lawrence Berkeley National Laboratory, One Cyclotron Road*
johan.gustafson@sljus.lu.se

Catalytic CO oxidation is a seemingly simple reaction between CO and O_2 molecules, one of the reactions in automotive catalytic converters, and the fruit-fly reaction in model catalysis. Surprisingly, the phase responsible for the catalytic activity is still under debate, despite decades of investigations. We have performed a simple but yet conclusive study of single crystal Rh and Pd model catalysts, resolving this controversy. For Rh, the oxygen covered metallic surface is more active than the oxide, while for Pd, thin oxide films are at least as active as the metallic surface, but a thicker oxide is less active. The difference between these oxide structures is that the thin PdO films expose coordinatively unsaturated (CUS) metal atoms that act as active sites, while Rh oxides and thicker PdO films do not expose such sites and are hence less active. Similar results have also been found for methane oxidation over Pd [1].

Under highly oxidizing conditions, which are, for instance, desirable for optimal efficiency of combustion engines, there is a general problem of deactivation of catalysts due to too high oxygen exposure, so-called oxygen poisoning. With the above results in mind, this problem is most likely related to the formation of oxides that do not expose CUS sites. We therefore believe that the problem of oxygen poisoning over Pd catalysts can be solved by growing a PdO film on top of a more inert metal such as Ag or Au, as this will limit the thickness of the oxide film and hence stabilize the active oxide surface.

In this presentation, we will discuss the active phase of Pd and Rh for CO oxidation, and hopefully show the first results of lower degree of oxygen poisoning over Pd/Au and Pd/Ag systems.

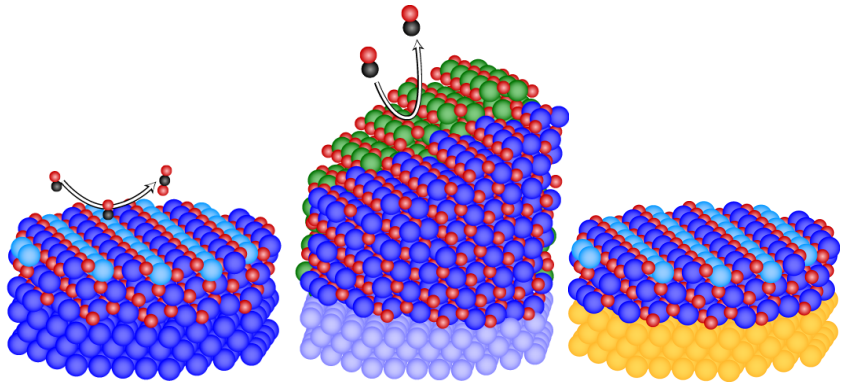

Figure 1 While a few-layer thick PdO(101) film is active for CO and methane oxidation, due to the active CUS sites, a thicker PdO film exposes inactive (100) surfaces. We want to stabilize the active PdO by growth on Au or Ag substrates.

References

1. A. Hellman et al., The active phase of palladiumduring methane oxidation. J. Phys. Chem. Lett. 2012, 3, 678–682.