

Extreme case of catalyst reconstruction: Adsorption and reaction-induced 3D nanoporosity

Cédric Barroo^{1,2,3}, Matthew M. Montemore^{2,3}, Austin J. Akey⁴, Efthimios Kaxiras^{2,5}, Juergen Biener⁶ and David C. Bell^{2,4}

¹*Chemical Physics of Materials and Catalysis, CP243, Université libre de Bruxelles, Belgium*

²*John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge MA USA*

³*Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA USA*

⁴*Center for Nanoscale Systems, Harvard University, Cambridge MA USA*

⁵*Department of Physics, Harvard University, Cambridge MA USA*

⁶*Nanoscale Synthesis and Characterization Laboratory, Lawrence Livermore National Laboratory, Livermore CA USA*
cbarroo@ulb.ac.be

The nanoscale Kirkendall effect has recently been shown to be an effective mechanism for the synthesis of hollow nanoparticles and nanotubes. Applying this same mechanism to create porosity in 3D bulk materials could prove useful, as bulk nanoporous materials have desirable properties. Various mechanisms for pore formation have been shown in previous work. Here, we show that oxidation of a bimetallic alloy can induce pore formation through the Kirkendall effect, wherein one of the constituents of the alloy has a higher net diffusion rate, resulting in vacancy injection and pore formation.

We indeed observed that low-temperature ozone treatment of a bulk Ag₇₀-Au₃₀ alloy induces large-scale compositional changes and induces isolated nanoporosity by Ag surface segregation via a vacancy mediated diffusion process. Further exposure to a methanol/O₂ mixture transforms the initial porosity to a bicontinuous open-porous structure with 50-70 nm pores that resembles the catalytically active nanoporous gold material made by wet chemistry dealloying. The forward movement of the Ag depletion front follows a square-root time dependence law but is many orders of magnitude faster than suggested by reported Ag self-diffusion data. Based on DFT and kMC simulations, we propose that the dramatic increase in the Ag diffusion rate is the consequence of an extremely high vacancy concentration that is caused by vacancy injection at the alloy/gas phase interface and reduces the activation barrier by ensemble effects. This is the first example of a nano-Kirkendall effect in a bulk material that leads to the formation of a complex 3D interconnected nanoscale porosity, and demonstrates that alloy catalysts can undergo surface reaction induced low-temperature, large scale compositional and morphological changes that can lead to irreversible catalyst degradation.

In addition to providing a novel route to nanopore formation, the results also suggest that dilute alloy catalysts with a more reactive minority component show enhanced stability against large scale compositional changes because of the lower rate of vacancy injection. Nanoporous alloy catalyst architectures are thus expected to provide improved compositional stability because the nano-confinement in nanoscale ligaments reduces the reservoir available for surface-induced phase segregation.

References:

[1] C. Barroo *et al.* J. Phys. Chem. C **121**, 5115 (2017).