

**Ostwald ripening or single atom trapping: towards understanding particle sintering**

X. Wang<sup>1,2</sup>, J. A. van Bokhoven<sup>1,2</sup>, D. Palagin<sup>2</sup>

<sup>1</sup>ETH Zurich, <sup>2</sup>Paul Scherrer Institut

Ostwald ripening, facilitated by the volatile species transport, is a leading cause of the platinum group catalysts degradation at high temperature in oxidizing atmosphere. However, the detailed understanding of Ostwald ripening is still missing, especially regarding the nature of volatile species, and the effect of support [1]. Recent experiments suggest that the volatile species can be trapped on ceria, forming atomically dispersed active catalytic sites instead of large nanoparticles [2], which typically form on non-reducible supports like alumina. To understand Ostwald ripening and atom-trapping phenomena at the atomic level, it is important to identify the stability and adsorption behaviour of volatile species, and their dependence on the local structure of different surfaces.

We conducted a comparative density functional theory study of the interaction of volatile species with various surfaces. PtO<sub>2</sub> species are the most likely volatile mobile species in the process of Ostwald ripening. Defect-free CeO<sub>2</sub>(111) and Al<sub>2</sub>O<sub>3</sub>(100) surfaces have a very small binding energy towards PtO<sub>2</sub> compared to the platinum surface, indicative of particle growth. However, the binding energy of PtO<sub>2</sub> on the step site of CeO<sub>2</sub>(111) surface is larger than that on the platinum surface. Therefore, the ceria stepped-edge could effectively trap the mobile species, generating atomically dispersed catalysts. The structure of trapped single-atom platinum-on-ceria catalysts is predicted to have a square-planar structure. A platinum atom in such a square-planar structure strongly binds to the surface, preventing the platinum atoms from aggregating into larger nanoparticles. Overall, the results indicate a mechanism of platinum particle growth in an oxidative atmosphere on defect-free alumina and ceria surfaces and of redispersion on the ceria surface with step-edges.

[1] S. B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, J. Sehested, S. Helveg, *J. Am. Chem. Soc.*, **2010**, 132, 7968-7975.

[2] J. Jones, H. Xiong, A. T. DeLaRiva, E. J. Peterson, H. Pham, S. R. Challa, G. Qi, S. Oh, M. H. Wiebenga, X. I. Pereira Hernández, Y. Wang, A. K. Datye, *Science*, **2016**, 353, 150-154.