

Using photoelectron spectroscopy to observe oxygen spillover to zirconia

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Supporting Information

The Interface Peak

Here, we shortly discuss the behavior of the interface layer with its separate XPS doublet which is visible for most 5-ML-thick tetragonal zirconia films.

The interface peak shifts in the opposite direction than the main peak (described in section 3.1 of the main paper); at high E_B (≥ 183 eV) of the main peak, it is a distinct peak with E_B between 180.7 eV–181.0 eV. At lower E_B of the main peak, it is a less distinct shoulder as in Figure 1a of the main paper, and becomes invisible when the main peak is located at ≈ 182.6 eV.

In summary, the Zr 3d doublet of the interface peak shifts to lower binding energies when the main peak's binding energy increases, i.e. with increasing reduction level. So, with an increased number of oxygen vacancies, the distance between main peak and interface peak increases, with a lower number of V_{Os} it decreases.

It is likely that the shift of the interface peak results from a changing number of oxygen vacancies at the interface. DFT calculations indicate that substrate–Zr bonds lead to the different binding energy of the interface layer [1]. Therefore, a higher number of V_{Os} can lead to a stronger bond between Rh and the Zr atoms surrounding the vacancy, thereby decreasing the binding energy further. (The Zr E_B at the interface becomes more metal-like.) A varying number of oxygen vacancies at the interface could also explain variations in the interface peak area observed by us (though near the confidence limit of peak fitting); with a lower number of V_{Os} present at the interface, less Zr atoms encounter a strong bond to Rh, and thus, a lower amount of Zr contributes to the interface peak.

[1] Li, H.; Choi, J.-I. J.; Mayr-Schmölzer, W.; Weilach, C.; Rameshan, C.; Mittendorfer, F.; Redinger, J.; Schmid, M.; Rupprechter, G. Growth of an ultrathin zirconia film on Pt₃Zr examined by high-resolution X-ray photoelectron spectroscopy, temperature-programmed desorption, scanning tunneling microscopy, and density functional theory. *J. Phys. Chem. C* **2015**, *119*, 2462–2470.