

We were supposed to study CO oxidation over Rh(553), but also wanted to test the large 2D detector that are being commissioned at ID03. We therefore started with the more simple Rh(111) system, and as it turned out we got very good results revealing the active phase of this model catalyst, which has been under debate for about 15 years.

The figure shows the main results, where the CO oxidation over Rh(111) has been activated, and the temperature is lowered slowly in order to follow the extinction. Panel A show the mass spectrometry signal of CO₂, and B shows the SXRD surface oxide signal. Three significant points are marked with vertical lines. The surface oxide signal drops throughout the measurements, but at point I, the drop becomes steeper, indicating that something has happened to the surface. After this point there are some oscillations in the catalytic activity, but it mainly stays high. At point II, the SXRD intensity seems to have reached 0, and the surface is metallic. The activity is still high, but the oscillations are stronger. Finally at point III, the catalyst dies. The fact that the oxide signal drops and disappears before the extinction of the catalyst unambiguously shows that the metallic surface is more active than the oxide.

The red line in the panel C, however, shows the SXRD surface oxide signal multiplied by 20. Although the signal is very weak, the oxide is clearly not completely gone until point III, when the catalyst becomes inactive. We interpret this as the metallic surface being more active than the oxide, but the oxide acts as a source of oxygen to the surface, hindering the CO from poisoning the surface. Hence both the metal and the oxide are crucial in the most active phase of Rh.

