

In-Situ ETEM Reveals Formation Mechanism of Single Pt Atom on Ru Nanoparticle Electrocatalysts for CO-Resilient Methanol Oxidation

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Single Pt atom catalysts on non-active carbon supports have been identified as key targets for electrochemical reactions because the high exposure of active Pt leads to record-high activities. For the methanol oxidation reaction (MOR) a PtRu alloy material is known as the most active catalyst, as the Ru atoms decrease CO poisoning of the active Pt. To combine the exceptional activity of single atom Pt catalysts with the benefits of an active metal support we must overcome the synthetic challenge of forming single Pt atoms on noble metal surfaces. Here, we have developed a process that grows and spreads Pt islands on faceted Ru branched nanoparticles to make single Pt atom on Ru catalysts [1]. Using high-speed atomic resolution in-situ environmental transmission electron microscopy (ETEM) studies, we reveal a spreading process as an effective concept for forming single Pt atom catalysts. The thermodynamically driven rearrangement of Pt islands on the Ru low index facets forms discrete Pt atoms on a Ru nanoparticle surface which display a very high resilience to CO-poisoning and generate record-high current density and mass activity.

To understand the formation of single Pt atoms from Pt islands, changes in the Pt structure were observed over time while heating the specimen in a hydrogen gas flow in an aberration corrected ETEM operating at 300 keV. Atomic resolution imaging was performed in-situ with a high-speed electron-counting direct detection camera (Gatan K3-IS). A partial pressure of 10 mbar H₂ was introduced to the ETEM, and the sample heated to 700 °C using a Protochips Aduro heating holder. Video was taken at 10 fps and the sample was delivered a low electron dose of just 106 e⁻/Å²/s. Drift correction was performed exclusively in GMS3 via cross-correlation using the IS player. A bandpass pre-filter was simultaneously applied to improve the cross-correlation. The experiment was carried out at a relatively low magnification of 69 kx, which enables a wide field of view to be captured with the K3 IS without losing lattice resolution. This allows capture of a statistically significant number of Pt island annealing events in a single region of interest.

Initially, small Pt islands were connected to the low index facets of the branched Ru nanoparticles by a neck of ~2 nm in diameter. The islands were stable and remained unchanged under electron beam irradiation. Upon in-situ heating and H₂ gas flow, the Pt started to spread across the Ru surface causing the height of the Pt island to decrease. As the islands continued to decrease in size, the contact area between Pt and the Ru nanoparticle surface increased. The spreading continued until the islands were no longer observable and Pt dispersed across the surface of the branched Ru nanoparticle. The in-situ studies revealed two thermodynamic drivers for the formation of single Pt atom catalysts; (i) The decrease in surface free energy of the Pt island as it spreads across the Ru surface. (ii) The increase in

the number of strong Pt-Ru bonds as more Pt atoms make contact with the Ru nanoparticle. The Pt-Ru bond formation is further supported by the crystallographic alignment of Pt atoms with the *hcp* Ru atomic structure, and atomic resolution STEM-XEDS.

Catalytic testing revealed the single Pt atoms on Ru catalysts achieve the highest current density and mass activity of any MOR catalyst reported to date. Theoretical calculations show the origin of these properties is the single Pt atom structure that limits CO poisoning [2].

References:

- [1] AR Poerwoprajitno et. al., Nature Catalysis, in press. DOI:10.1038/s41929-022-00756-9
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