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The Role of Morphology in Promoting Self-healing in Cobalt Nanomaterials¹

JASON HATTRICK-SIMPERS, University of South Carolina

Oxidative corrosion is a ubiquitous degradation mechanism that cuts across the entire landscape of materials science, surface science, chemistry, and surface physics. In the case of transition metal nanomaterials, oxidation often proceeds rapidly to completion, and obscures the unique properties associated with the metals. Here we use operando Raman and X-ray absorption fluorescence spectroscopic studies to demonstrate that cobalt nanorods exposed to oxidative conditions exhibit substantially different oxidation properties compared to their nanosphere analogs. In particular, in the case of the nanorods an oscillatory oxidation/reduction behavior is observed that preserves the metal surface of the nanomaterial indefinitely. This behavior is confirmed by Fischer-Tropsch (FT) catalysis studies, which clearly demonstrate that as opposed to the nanospheres, which oxidize rapidly in the presence of moisture, FT reactions on cobalt nanorods are unperturbed by water in the feed. High-resolution transmission electron microscopy studies reveal that the differences in oxidation behavior observed stem from the crystallographic faceting of the respective nanomaterials. In particular, the {110} planes exposed by the cobalt nanorods present the readily reducible Co^{3+} ions at the surface of the nanomaterial, effectively promoting reduction of the oxide during its growth.

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