

Exposure of Pd-based hydrogen purification membranes to H₂S, a common contaminant in coal gasification streams, can cause membrane performance to deteriorate, either by deactivating surface sites required for dissociative H₂ adsorption or by forming a low-permeability sulfide scale. In this work, the composition, structure, and catalytic activity of Pd₄S, a surface scale commonly observed in Pd-membrane separation of hydrogen from sulfur-containing gas streams, were examined using a combination of experimental characterization and density functional theory (DFT) calculations. A Pd₄S sample was prepared by exposing a 100 *nm* Pd foil to H₂S at 908 K. Both X-ray photoemission depth profiling and low energy ion scattering spectroscopic (LEISS) analysis reveal slight sulfur-enrichment of the top surface of the sample. This view is consistent with the predictions of DFT atomistic thermodynamic calculations, which identified S-terminated Pd₄S surfaces as energetically favored over corresponding Pd-terminated surfaces. Activation barriers for H₂ dissociation on the Pd₄S surfaces were calculated. Although barriers are higher than on Pd(111), transition state theory analysis identified reaction pathways on the S-terminated surfaces for which hydrogen dissociation rates are high enough to sustain the separation process at conditions relevant to gasification applications.