

The First-Principles approach to the interplay of Ligand Effect in Enhanced Dehydrogenation of HCOOH on the Bimetallic Pd-M Catalyst

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The critical role of the Ag-Pd ligand effect (which is tuned by changing the number of Pd atomic layers) in determining the dehydrogenation and dehydration of HCOOH on the bimetallic Pd/Ag catalysts was elucidated by using the spin-polarized density functional theory (DFT) calculations. Our calculations suggest that the productivity and selectivity to H₂ production from HCOOH on the bimetallic Pd/Ag catalysts strongly depends on the Pd atomic layer thickness at near surface. In particular, the thinnest Pd monolayer in the Pd/Ag system is responsible for enhancing the dehydrogenation of HCOOH toward H₂ production by reducing the surface binding strength of specific intermediates such as HCOO and HCO. The dominant Ag-Pd ligand effect by the substantial charge donation to the Pd surface from the subsurface Ag [which significantly reduce the density of state (particularly, d_{z²-r²} orbital) near the Fermi level] proves to be a key factor for the enhanced kinetics of dehydrogenation, whereas the expansive (tensile) strain imposed by the underlying Ag substrate plays a minor role. This work hints on the importance of properly engineering the surface activity of the Ag-Pd core-shell catalysts by the interplay between ligand and strain effects.