

Adsorption of Pd and Au over Fe₃O₄(001) surface

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In order to understand the catalytic activity of magnetite supported palladium and gold catalysts, the adsorption configurations and energies of single Pd and Au atoms on the Fe₃O₄(001) surfaces were studied using density functional theory based GGA+U calculations. Various adsorption sites for Pd and Au atoms on 9-layer and 17-layer slabs were considered, from which two strongly favored geometries emerged. Gold atoms prefer to be linearly coordinated to two surface oxygen atoms (as in the case of Cu₂O). This is facilitated in a tilted geometry, in which one surface oxygen atom relaxes into the surface and one relaxes outward; gold is accommodated in the surface plane. Palladium is also twofold coordinated to surface oxygens in a bent molecular geometry, therefore protrudes from the surface; the oxygen atoms remain in the surface plane. Both adsorbates are positively charged, resulting in reduced magnetic moments and altered orbital occupancies on iron atoms. In addition, the effect of CO addition was investigated, and found to differ significantly for two precious metals. CO binds weakly to Au, but strongly to Pd, having a strong effect on the Pd-surface geometry and the electronic structure. The activation barriers that clarify possible diffusion pathways were calculated for both adsorbates.

