In this work we present the results of the analysis of the surface structures and absorption properties with respect to the CO and O_2 molecules of the Sn/Rh and Rh/SnO_2 model systems. In the part dedicated to the Sn structures on Rh surfaces with two different orientations — Rh(110) and Rh(111) — we have investigated the development of the core electron levels and valence band during the development of surface reconstructions and absorption of CO molecules. The surface reconstructions of the Sn/Rh(110) systems were studied for the first time. Difference in behaviour w.r.t. Sn/Rh(111) was observed and explanation offered. Finally, on in-situ prepared epitaxial SnO_2 layers, the surface reconstruction (4×1) was observed. The CO adsorption properties of Rh on polycrystalline and epitaxial SnO_2 layers were also studied and difference in behaviour explained.