Bimetallic Rh–V system was studied by means of surface science experimental methods. Properties of ultra-thin Rh–V layers supported by γ-Al$_2$O$_3$ were compared with model systems prepared by vacuum V deposition on Rh(111), Rh(110) and polycrystalline rhodium. Formation of ordered V–Rh(111)–(2×2), V–Rh(110)–(2×1) and V–Rh(110)–(1×2) subsurface alloys and their electronic and atomic structure were investigated and models of the surface reconstructions were proposed. Influence of the subsurface alloy formation on interaction with CO and O$_2$ molecules as well as the influence of the molecule adsorption on this alloy was investigated. The bond between CO molecules and Rh–V alloy surface was weakened due to pronounced changes in surface valence band structure. Oxygen which adsorbed on the alloy surface reacted with the subsurface vanadium at elevated temperature and blocked the interaction of the metal substrate with CO molecules.