

Palladium Catalysts: General Notes

Palladium is of exceptional interest to theoretical chemists and researchers in the field of catalysis because it is the only element with the electronic configuration $d^{10}s^0p^0$, which can vary depending on the type of chemical bonding and defines the specific behavior of this metal.

It is well known that on the metal surface can be at least four forms of hydrogen with different reactivity in liquid-phase hydrogenation processes: weakly bound molecular $H_2^{\delta+}$, strongly bound atomic hydrogen: ionized $H^{\delta+}$, $H^{\delta-}$ and non-ionized H, between which adsorption equilibrium is established. In addition to the indicated forms, dissolved hydrogen is present in the bulk of palladium, which penetrates its crystal lattice through areas that adsorb weakly bound molecular forms (heat of adsorption is $7 \text{ kJ} \times \text{g-atom}^{-1}$). Dissolution of hydrogen in palladium is energetically more favorable (activation energy $15 \text{ kJ g-atom}^{-1}$) than its migration along the surface to centers with a higher heat of adsorption (activation energy $55 \text{ kJ g-atom}^{-1}$). When hydrogen dissolves, multicenter binding of hydrogen with palladium can occur, so for example, for Pd/Al₂O₃, up to 5 hydrogen atoms are adsorbed on one Pd atom.⁵ Hydrogen on the surface of metals can exist in a “pre-dissociative form”, in which the H-metal bond is stronger than the H-H bond.^{6,7} The charge in Pd clusters is distributed among all atoms. Clusters with n=4 are electrically neutral. The maximum charges in absolute value (-0.014, -0.008, and -0.011 a.u.) have the central atoms in clusters with a planar structure of Pd₅, Pd₆, and Pd₇. In the most stable clusters with high symmetry, the electron density is distributed more uniformly and the charge on the atoms does not exceed +0.005 a.u. The state of adsorbed hydrogen can be related to the location of the adsorption center in the Pd crystal. For example, it was shown that hydrogen is adsorbed only dissociatively on the low-index Pd (111), (100), and (110) faces, while molecular hydrogen can also be present on the Pd (100) face.⁸ On the stepped Pd (210) surface, both hydrogen atoms and their molecules are chemisorbed.

It is characteristic that on the free surface the H₂ molecule dissociates spontaneously, without overcoming the energy barrier, and on the surface filled with hydrogen, an activation barrier appears, and hydrogen can exist in a chemisorbed metastable molecular state. Atoms of dissociatively adsorbed hydrogen can be electrically neutral and also carry a partial positive or negative charge, depending on the position of the adsorption center on the Pd surface (Fig.-1).⁹

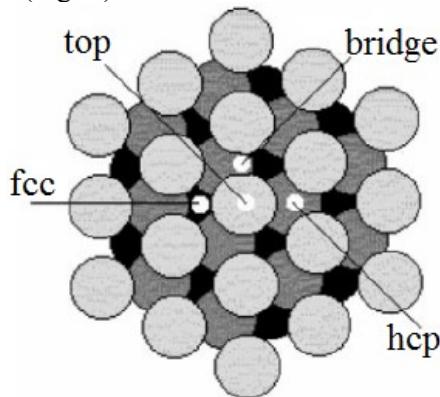


Fig.-1: Three-layer Model of the Pd Surface and the Location of Adsorption Centers⁹

The adsorption of nitro compounds under conditions of liquid-phase hydrogenation occurs on the catalyst surface, on which hydrogen and solvent are already present.^{10,11} This is the reason for the competitive and displacement nature of adsorption of reagents and solvent. Nitrobenzene is strongly chemisorbed on platinum group metals and, in particular, on palladium.¹² The adsorption capacity of hydrogen decreases in the series Pt > Ru > Ir > Pd > Rh > Os. When nitrobenzene is hydrogenated on palladium black in a water-alcohol medium, an adsorption film is formed on the catalyst surface from nitrobenzene molecules and the products of its incomplete reduction, the desorption of which into the solution is very limited. Nitro compounds are adsorbed on group VIII metals by nitrogen and oxygen atoms of the nitro group and create a positive charge on the catalyst surface. In this case, the formation of nitrobenzene radical anions is possible. Products of incomplete reduction of nitrobenzene are adsorbed mainly by nitrogen and oxygen atoms of functional groups. Aniline is not adsorbed in the presence of a nitro group.