

The model of nitrobenzene and the products of its incomplete hydrogenation has been simulated on the surface of Pd<sub>6</sub> clusters by optimizing the geometry of the Pd – substrate system with some predetermined structural characteristics by the Hartree-Fock (HF) method in the SBKJC valence basis using the effective core potentials of Stevens-Basch-Krauss-Jasien-Kundari (ECP SBKJC) for the chemical elements Li-Rn.<sup>13</sup> Fig.-2 shows the optimized structures of nitrobenzene, nitrosobenzene and phenylhydroxylamine on the surface of a flat palladium cluster.

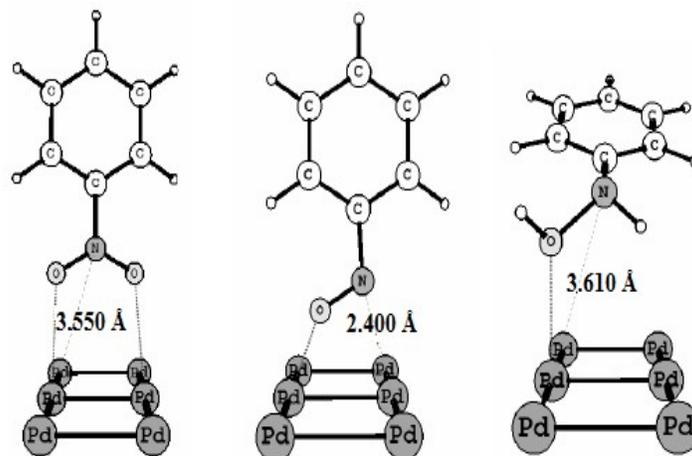


Fig.-2: The Optimized Structures of Nitrobenzene, Nitrosobenzene and Phenylhydroxylamine on the Surface of a Flat Palladium Cluster<sup>13</sup>

The modeling of clusters applied to activated carbon showed that Pd forms particularly strong bonds with unsaturated carbon atoms.<sup>14</sup> As the cluster size increases, the strength of Pd-C bonds increases. With a low content of palladium, its atoms on the surface of the coal are positively charged due to the strong donor-acceptor interaction with the p-system of the substrate. With an increase in the Pd concentration, the deficit of the 4d electron density decreases and the positive charge of the palladium atoms decreases.<sup>15</sup>

### Selective Hydrogenation of Aromatic Nitro Compounds on Palladium-containing Catalytic Systems

The significance and role of palladium in catalytic processes are largely related to the structure of active centers on its surface.<sup>15-19</sup> Palladium-containing catalysts differ significantly in properties from catalytic systems based on other metals of the platinum group, as well as Ni or Cu. Pd-based catalysts are one of the most effective catalytic systems for the hydrogenation of double (also conjugated) and triple bonds. In cases where it is necessary to hydrogenate only nitro groups in aromatic nitro compounds, without affecting the double bonds of the aromatic ring, it is necessary to use Pd-systems.

If an aromatic nitro compound contains halogen-containing groups in a molecule, it is necessary to selectively hydrogenate the nitro group bypassing the hydrogenolysis of the C – Cl bond.<sup>18</sup> This goal is very difficult to achieve since palladium-containing catalysts are considered the best catalysts for dehalogenation. There are reports on the selective hydrogenation of fluorinated nitrobenzenes on pure palladium catalysts. Chloronitrobenzenes can be selectively hydrogenated to amines on palladium catalysts without hydrogenolysis of the C – Cl bond with the addition of triphenyl phosphite. The hydrogenation of chloronitrobenzenes with a high yield of amines (up to 98%) was carried out on a Pd / C catalyst, first treated with sulfoxide and then with hydrazine. The highest selectivity (98%) was revealed on the large particles, on which the adsorption of chloronitrobenzenes was the strongest.

Palladium supported catalysts with platinum and rhodium added showed high hydrogenation selectivity when reduced as nitro groups as well as the aromatic ring in nitrobenzene in the liquid phase.<sup>3,4,12,16-21</sup> The correct choice of the catalyst composition is very important in the competitive hydrogenation of compounds with different functional groups, in the case of hydrogenation of di- and polynitro compounds, as well as in the case of the likelihood of hydrogenation of both nitro groups and the aromatic ring.<sup>22</sup>