SUPPORTED PALLADIUM CATALYSTS FOR SELECTIVE LIQUID-PHASE HYDROGENATION OF AROMATIC NITRO COMPOUNDS

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ABSTRACT
This article is devoted to the issues of aromatic hydrogenation reactions on supported palladium catalysts: adsorption on palladium catalysts, models of the Pd surface and the location of adsorption centers, features of hydrogenation of aromatic nitro compounds over palladium catalysts with additives of rare-earth elements. Palladium catalysts for hydrogenation of nitro groups in nitro compounds with different functional groups are described. The article discussed theoretical and experimental aspects of data from literature and patent sources. The experimental results of the authors of this article concerning selective hydrogenation of 4,4'-dinitrostilbene-2,2'-disulfonic acid to 4,4'-diaminostilbene-2,2'-disulfonic acid are also shown. Pd-Cu/sibunite was used for selective obtaining 4,4'-diaminostilbene-2,2'-disulfonic acid in water. The formation on the surface of mixed active centers of the type of solid solutions of the Cu₃Pd composition with a particle size of 5 nm and massive Pd clusters of 100 nm is established, which cause sufficient uniformity of both the surface and the adsorbed hydrogen. This is probably the reason for the high selectivity of the Pd-Cu/sibunite catalyst in the hydrogenation of 4,4'-dinitrostilbene-2,2'-disulfonic acid. A highly selective Pd-Cu / sibunite catalyst has been developed, the optimal conditions for the process (temperature and pressure of hydrogen, solvent) have been determined, which make it possible to obtain the target amine, 4,4'-diaminostilbene-2,2'-disulfonic acid, up to 91-92%. The optimal composition of the catalyst is stable when hydrogenating 7-8-fold portions of 4,4'-dinitrostilbene-2,2'-disulfonic acid.

Keywords: Liquid-phase Hydrogenation, Aromatic Nitro Compounds, Palladium Catalysts, Rare-earth Elements, 4,4'-dinitrostilbene-2,2'-disulfonic Acid, Sibunite.

INTRODUCTION
In recent years, the interest of chemists in the study of selective catalytic transformations of various organic compounds that lead to the production of valuable chemical products, in particular, to the reduction of aromatic nitro compounds to amines, has grown significantly. The hydrogenation reaction in the liquid phase of aromatic nitro compounds occupies a special place among the chemical reactions of nitro compounds.¹⁻⁴ Platinum group catalysts on various supports play an important role in these processes. Catalysts based on platinum group metals, despite their high cost, are widely used to obtain aromatic amines from the corresponding nitro compounds. Researchers from many scientific teams around the world are not even stopped by the high cost of catalysts based on platinum group metals, since such catalytic systems demonstrate high activity and selectivity. A special role in this is played by palladium-based catalysts on various supports.
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^{δ+}, strongly bound atomic hydrogen: ionized H^{δ+}, H^{δ-} 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 kJ×g-atom\(^{-1}\)). Dissolution of hydrogen in palladium is energetically more favorable (activation energy 15 kJ g-atom\(^{-1}\)) than its migration along the surface to centers with a higher heat of adsorption (activation energy 55 kJ g-atom\(^{-1}\)). When hydrogen dissolves, multicenter binding of hydrogen with palladium can occur, so for example, for Pd/Al_2O_3, 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 Pd_5, Pd_6, and Pd_7. 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 H_2 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).\(^9\)

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.
The model of nitrobenzene and the products of its incomplete hydrogenation has been simulated on the surface of Pd₆ 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. 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

The modeling of clusters applied to activated carbon showed that Pd forms particularly strong bonds with unsaturated carbon atoms. 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.

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. 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. 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 phosphate. 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. 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.
Hydrogenation can be stopped at intermediate stages.\textsuperscript{21,22} Thus, the reduction of nitrobenzene to Pd / C in an alkaline medium leads to the formation of hydrazobenzene in a yield of 93-97% and purity of 99.5 - 99.7%. Hydrogenation of o-mononitrotoluene in an alcohol medium with a Pd catalyst at 30-150°C in the presence of bases leads to the formation of hydrazotoluene. Similarly, o-hydrazotoluene is obtained in a yield of more than 80% in the presence of sodium hydroxide and quinone. The presence of alkali contributes to the acceleration and selectivity of the reaction, and quinone inhibits further reduction; the dielectric constant of the solvent exerts a strong influence on the process. When nitro compounds are reduced by hydrogen with Pt/C or Pd/S/Se/C catalysts in the methylmorpholine medium at 28-30°C, the process stops at the hydroxylamine stage (in the reduction of o-nitrotoluene, the content of o-tolyl hydroxylamine in the reaction product reaches 96%). As a solvent, methylpiperidine and dimethyl sulfoxide are also used.\textsuperscript{17,22,23} Platinum and palladium catalysts deposited on coal showed high activity and stability in the reduction of nitrobenzene, nitroanilines, p- and o-nitrophenols and other nitro compounds with various substituents.\textsuperscript{17-22}

**Palladium Catalysts with Additives of Rare-earth Elements**

Recently, to improve the processes of organic and inorganic synthesis, catalysts based on rare-earth elements (REE) are increasingly being used by different scientific schools. The catalyst sub-industry consumes about 25% of all REE. The transition metals of the lanthanum group, as well as scandium and yttrium, are used in various fields of modern technology: in radio electronics, instrument making, nuclear technology, mechanical engineering, the chemical industry, and metallurgy. The REE market has been developing significantly in recent years; the world demand for REE is regularly increasing.\textsuperscript{24} The content of rare earth elements in the earth’s crust is high and represents a significant material base in various industries. Rare earth elements are used as an active phase, a promoting additive, and their oxides as a carrier.\textsuperscript{25-27}

Rare earth elements can be added to increase the activity and stability of Pd and Pt catalysts in the hydrogenation of nitro compounds.\textsuperscript{28-34} Thus, it was revealed that the specific catalytic activity of Pd catalysts promoted with REE in the hydrogenation reactions of nitro compounds is 2 orders of magnitude higher than on Pd/Al\textsubscript{2}O\textsubscript{3}. Within the group of lanthanides, the highest specific activity was found to be characteristic of the central elements (Eu, Ga, Tb).

Rare-earth elements are used as an active phase, promoting additives, and their oxides as a carrier.\textsuperscript{12,17,26} It is pointed out that one of the directions of use of rare and platinum metals is associated with the development of catalysts for various purposes.

Hydrogenation of nitrobenzene on 1% Pd deposited on rare earth element oxides Ce, Pr, Nd, Sm, Eu, Cd, Tb, Dy, Ho, Tm, Yb, Lu was studied and compared with Pd/Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{31} It was shown that Eu\textsubscript{2}O\textsubscript{3}, Yb\textsubscript{2}O\textsubscript{3}, and Tb\textsubscript{2}O\textsubscript{3} were the most active carriers of all oxides. The activity of catalysts on REE oxides exceeds that of Al\textsubscript{2}O\textsubscript{3} by 1.2-4 times. The authors explain the high activity of these catalysts by the influence of REE oxides on the formation of active centers of palladium catalysts.

The efficiency of catalytic systems based on 5% Pd - 5% OREE (where OREE are oxides of rare earth metals - lanthanum, europium, gadolinium, and terbium) for hydrogenation of p - nitrotoluene to p-toluidine was studied. The authors have applied α-Al\textsubscript{2}O\textsubscript{3} and 6% γ-Al\textsubscript{2}O\textsubscript{3} / α-Al\textsubscript{2}O\textsubscript{3} as carriers. It was found that the addition of OREE to 6% γ-Al\textsubscript{2}O\textsubscript{3} / α-Al\textsubscript{2}O\textsubscript{3} causes a decrease in the specific surface area of the support, and the addition of OREE to α-Al\textsubscript{2}O\textsubscript{3} increases the surface area. It should be noted that the addition of terbium oxide for both types of carriers showed the best results. Thus, in the case of the α-Al\textsubscript{2}O\textsubscript{3} support, the increase in the specific surface area turned out to be the largest: from the initial value of 0.20 m\textsuperscript{2}/g, with the addition of terbium oxide, the specific surface area increased to 3.96 m\textsuperscript{2}/g. If a 6% γ-Al\textsubscript{2}O\textsubscript{3} / α-Al\textsubscript{2}O\textsubscript{3} support was used, then the decrease in the specific surface area was the smallest in comparison with other modifying additives (12.51 m\textsuperscript{2}/g), with the initial value of the specific surface area being 19.04 m\textsuperscript{2}/g. The specific surface area in the case of using other modifying additives was more than 10 m\textsuperscript{2}/g.\textsuperscript{32-34} The authors concluded that the promotion of the initial aluminum oxide carrier by adding OREE leads to a significant increase in the rate of hydrogen absorption in the hydrogenation reaction. According to the conclusions of some scientists, a significant influence of the modifier on the activity of
the catalytic system is associated with the presence of REE aluminate crystals formed during firing at the interface.\textsuperscript{33,34}

Hydrogenation of o-nitroanisole to o-aminoanisole was studied on 1\% palladium catalysts containing holmium and aluminum oxides. The starting nitro compound, o-aminoanisols are widely used in the aniline paints, chemical-pharmaceutical and food industries. It is known that the o-nitroanisole molecule contains a methoxy group, has a negative induction effect and a positive mesomeric effect. It was found that the rate of hydrogenation of o-nitroanisole on 1\% Pd/Ho\textsubscript{2}O\textsubscript{3} catalyst exceeds the rate of hydrogenation on 1\% Pd/Al\textsubscript{2}O\textsubscript{3} by 2.8 times, which shows a greater activity of 1\% Pd/Ho\textsubscript{2}O\textsubscript{3} catalyst.\textsuperscript{34}

The study of the dependence of the reaction rate of the hydrogenation of nitrobenzene and o-nitroanisole on 1\% Pd catalysts containing OREE from the nature of OREE (which is associated with the structure of the electron shell of the elements of the lanthanide series) shows that palladium catalysts OREE, which begin and end the series of lanthanides, have lower activity compared to catalysts containing OREE located in the central part of the lanthanide series (Fig.-3). 1\% Pd/Lu\textsubscript{2}O\textsubscript{3} and 1\% Pd/Pr\textsubscript{2}O\textsubscript{3} exhibit low activity in the series of 1\% Pd catalysts containing OREE, but their activity is 1.3 times higher than that of the catalyst based on Al\textsubscript{2}O\textsubscript{3}. So, replacing the usual carrier Al\textsubscript{2}O\textsubscript{3} with a rare earth oxide gives an increase in the rate of nitrobenzene hydrogenation from 1.3 (Lu\textsubscript{2}O\textsubscript{3}) to 4.5 times (Tb\textsubscript{2}O\textsubscript{3}); in the hydrogenation of o-nitroanisole, from 1.9 (Yb\textsubscript{2}O\textsubscript{3}) to 3.6 times (Gd\textsubscript{2}O\textsubscript{3}). In the case of nitrobenzene hydrogenation, the 1\% Pd/Tb\textsubscript{2}O\textsubscript{3} catalyst has the highest activity and 1\% Pd/Gd\textsubscript{2}O\textsubscript{3} in the case of o-nitroanisole hydrogenation.

![Fig.-3: The Rate of the Hydrogenation Reaction of Nitrobenzene (1) and o-nitroanisole (2) on 1\% Pd Catalysts Containing Various Oxides of Rare Earth Elements and Al\textsuperscript{27,31,34}]

RESULTS AND DISCUSSION

Palladium Catalysts for Hydrogenation of Nitro Groups in Nitro Compounds with Functional Groups

In literature, the effect of copper on the catalytic properties of a palladium catalyst (5 wt. \%) during the hydrogenation of o-, m-, and p-nitrochlorobenzenes has been written in some works.\textsuperscript{17} The authors found that the addition of copper to the palladium catalyst decreases the hydrogenating activity of the original catalyst, but when the optimal amount of copper is added to the palladium (<2 at. \%) the reaction of chlorine elimination is practically close to zero, while the rate of reduction of the nitro group at pressures of 4.0-10.0 MPa is still at a high level.

Catalysts based on deposited palladium catalysts with copper additives have also shown high selectivity in hydrogenation of nitro groups in nitro compounds with functional groups.\textsuperscript{35}

We have researched supported catalysts based on palladium with different additives (Rh, Ru, Cu, Pt) in the processes of hydrogenation of simple molecules (nitrobenzene, aniline, benzene) and aromatic nitro compounds with one or two nitro groups and different functional groups. For investigation of the high-pressure kinetic installation, the main part of which is or the “duck” made of steel or an improved Vishnevsky autoclave made of titanium has been used. The experiment was carried out according to the method described earlier.\textsuperscript{19,36-38} Liquid phase hydrogenation of aromatic nitro compounds has been studied under the pressure of hydrogen with a variation of temperature, solvents and catalysts composition.

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Thus the catalysts with composition Pd-Cu/sibunite were active in a case of selective obtaining 4,4’-diaminostilbene-2,2’-disulfonic acid (DAS) by hydrogenation of 4,4’-dinitrostilbene-2,2’-disulfonic acid (trans-DNS) in water. The product of the reaction, amine, 4,4’-diaminostilbene-2,2’-disulfonic acid (DAS) is used in photographic technology to produce phosphorescent whiteners for fibers and paper and as a bleach.

The starting molecule contains functional groups and C = C-multiple bonds. In the initial DNS, either two NO\(_2\) groups can be reduced with the formation of a diamine and a C = C bond, with the formation of dibenzyl derivatives, destruction of the stilbene bond with the formation of p-aminotoluene sulfonic acid. Alternatively, hydrogenolysis of the sulfo groups is also possible. Therefore, the development of catalysts for the selective reduction of DNS for the preparation of DAS in a high yield is very important both from a theoretical and practical point of view.

We have known that the simultaneous hydrogenation of both the nitro groups and the stilbene C=C bond occurs on Pd catalysts deposited on sibunite and Al\(_2\)O\(_3\). X-ray diffraction and electron microscopy (Fig.-4a, b) have demonstrated that Al\(_2\)O\(_3\) has a stronger interaction with the active phase compared to sibunite, which causes a higher activity of aluminum oxide during the hydrogenation of DNS. The formation on the surface of mixed active centers of the type of solid solutions of the Cu\(_3\)Pd composition with a particle size of 5 nm and massive PD clusters of 100 nm is established, which causes sufficient uniformity of both the surface and the adsorbed hydrogen. This is probably the reason for the high selectivity of the Pd-Cu/sibunite catalyst in the hydrogenation of DNS (Fig.-4c).

The addition of copper to palladium in an amount of more than 3:7 significantly reduces the rate of hydrogenation of the DNS up to a complete stop. Varying the copper content from 1 to 3 decreases the reaction rate, but increases the selectivity of the process. The optimal catalyst Pd-Cu/sibunite allows to reach the maximum yield of the desired product is up to 91-92% in an aqueous medium. The developed catalyst is stable during hydrogenation of 7-8-fold portions of DNS.

**CONCLUSION**

The possibility of using nitro compounds in industry and agriculture as relatively inexpensive chemicals in the production of various valuable chemical products is currently attracting chemists. A special place among the chemical transformations of nitro compounds is occupied by the hydrogenation reaction in the liquid phase up to aromatic amines. In a frame of short review adsorption of nitro compounds under conditions of liquid-phase hydrogenation using palladium catalysts, theoretical and experimental aspects of data from literature and patent sources are discussed. The authors also have described their experiments with the selective hydrogenation of 4,4’-dinitrostilbene-2,2’-disulfonic acid over Pd-Cu catalysts.
deposited on sibunite and Al₂O₃ to obtain 4,4'-diaminostilbene-2,2'-disulfonic acid. A highly active stable catalyst Pd-Cu / sibunite has been developed, the optimal conditions for the process (temperature and pressure of hydrogen, solvent) have been determined, which ensure the production of 4,4'-diaminostilbene-2,2'-disulfonic acid with a yield of 91-92%. The developed catalyst is stable when hydrogenating 7-8-fold portions of 4,4'-dinitrostilbene-2,2'-disulfonic acid.

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