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**Title: SUPPLIED PALLADIUM CATALYSTS AND METHODS OF THEIR SYNTHESIS**

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## SUPPLIED PALLADIUM CATALYSTS AND METHODS OF THEIR SYNTHESIS

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**Abstract:** However, among all the metals of the platinum group, it is palladium that is most often used in selective hydrogenation catalysts, since it demonstrates 100% selectivity in the hydrogenation of acetylenes and dienes to alkenes. The researchers suggest that this is due to the different adsorption and desorption energies of alkynes and alkenes on palladium and platinum.

**Keywords:** hydrogenation, palladium, adsorption and desorption energies.

### Introduction

Currently, various supported catalysts are used in industry as selective hydrogenation catalysts, which make it possible to increase the surface of the active component, prevent sintering, and save expensive metal. Platinum group metals Pt, Rh, Ru, Pd [1] supported on carbon, aluminum oxide, silicon oxide and other carriers are used in industry as active components of supported catalysts for hydrogenation of multiple carbon-carbon bonds. In addition to platinum group metals, copper, cobalt, nickel are also used, deposited on various carriers. However, among all the metals of the platinum group, it is palladium that is most often used in selective hydrogenation catalysts, since it demonstrates 100% selectivity in the hydrogenation of acetylenes and dienes to alkenes. The researchers suggest that this is due to different energies of adsorption and desorption of alkynes and alkenes on palladium and platinum [1]. DFT calculations (based on density functional theory) showed that, during hydrogenation, alkenes-intermediates form  $\pi$ -adsorption with the palladium surface, while platinum is characterized by the formation of di- $\sigma$ -adsorption. Due to the stronger interaction with platinum, the alkene is not desorbed and is hydrogenated to the alkane. A large number of studies indicate that palladium is most characterized by  $\pi$ -adsorption [2]. Some researchers demonstrate that palladium alkene selectivity in alkynes hydrogenation is also

associated with a stronger metal-hydrogen bond than other metals such as Pt and Rh, which prevents further hydrogenation of the hemihydrogenated intermediate.

At the dawn of petrochemistry, selective hydrogenation catalysts were synthesized by depositing a solution of an active metal compound on a porous support, and catalytically active metal particles after reduction, as a rule, were formed inside the support (Fig. 1).

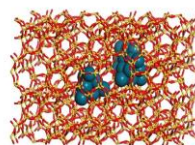


Fig. 1. Model of a palladium catalyst based on ZSM-5 with Pd particles in the pores of the support

In this case, there are diffusion restrictions for the reacting substrate, which play an important role in selective hydrogenation. In order to react, the substrate must pass through the pores of the carrier and be adsorbed on the active sites of the catalytically active component (metal). Since diffusion is the limiting stage in the catalytic act, then in order to increase the reaction rate, it is necessary to increase the diffusion rate. An increase in the diffusion rate can be achieved if the catalytically active component (metal) is located on the outer surface of the support, and not inside the pores (Fig. 2). For this purpose, special "egg-shell" -type catalysts (crust type) have been developed, which are a carrier (tablets, spherical granules made of, for

example, aluminum oxide, several millimeters in size) with a thin layer of the active component applied to the outer surface (Fig. 2) [3]. The thickness of the active layer of the carrier with the active component applied is about 50-250  $\mu\text{m}$ . Pd is often used in industry as an active component because of its high selectivity to olefins in the hydrogenation of acetylenic and diene hydrocarbons. The palladium content in such catalysts ranges from 0.05 to 0.5 wt. %.

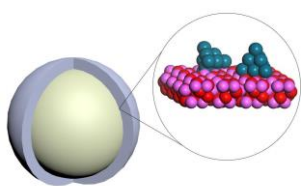


Fig. 2. Egg shell catalyst

The use of egg-shell catalysts makes it possible to increase the rate of mass transfer of the substrate to the active centers of the catalyst [3]. Another advantage of egg-shell catalysts is the increased selectivity of the target product. For example, in the case of the hydrogenation of acetylene on a classical catalyst, where the active metal is inside the support, due to diffusion restrictions, it is more difficult for ethylene to leave the catalyst particle, which leads to further hydrogenation to ethane and, as a consequence, to a decrease in the selectivity to ethylene. The dependence of the selectivity on the penetration depth of the active component was studied in [3] using the example of acetylene hydrogenation over a Ni /  $\text{Al}_2\text{O}_3$  catalyst. It has been shown that the maximum selectivity for ethylene is achieved when using an eggshell catalyst with a thin layer of the active component (moreover, the selectivity decreases in the row egg shell with a thin layer of the active component > egg shell with the penetration of the catalyst deep into the support > catalyst obtained by impregnation and distribution of the active component inside carrier > "egg yolk" -catalyst with an active component inside the carrier and the absence of a catalyst on the outer surface). Egg-shell catalysts are currently used in many selective hydrogenation processes.

There are various methods for synthesizing supported catalysts, for example, impregnation, co-deposition, photodeposition [4]. Among these methods, impregnation with compounds of the active component of the finished support is one of the main methods for the synthesis of supported catalysts both in industry and in laboratories. In this method, the carrier with the specified properties is prepared separately. The distribution of the active ingredient in the carrier can be controlled. Thus, the method of impregnation with solutions of  $\text{PdCl}_2$  and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  obtained monometallic Pd /  $\text{SiO}_2$  and CaPd /  $\text{SiO}_2$  catalysts of the "egg-shell" type. A palladium catalyst supported on activated carbons obtained by various methods was obtained by impregnating carbons with solutions of  $\text{H}_2\text{PdCl}_4$ ,  $\text{Pd}(\text{OAc})_2$ ,  $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$ . In [4], a palladium catalyst based on a mesoporous carbon material was obtained by direct synthesis using tetraethylorthosilicate, sucrose, and a palladium salt, followed by carbonization and removal of the  $\text{SiO}_2$  template using HF. A 5% palladium catalyst supported on a mesoporous carbon support obtained using a non-rigid template was synthesized by impregnating a previously prepared support with an  $\text{H}_2\text{PdCl}_4$  solution [5].

However, there are difficulties in this approach. During impregnation, undesirable components, for example chloride ions, can be adsorbed on the active sites of the catalytically active metal, reducing the catalytic activity. On the other hand, the impregnation method involves many stages and the need to control the physical and chemical properties of the solution, which makes the method laborious.

The most attractive from the point of view of direct metal deposition on a support without using solutions of metal compounds are physical methods, for example, electron beam, magnetron, chemical vapor deposition (CVD process), metal-vapor synthesis, etc. [6]. Physical methods allow the direct deposition of a catalytically active metal on the surface of the support, and avoid the adsorption of undesirable impurities on the catalyst during synthesis. In the course of synthesis, much less

waste is generated compared to classical methods of catalyst synthesis. However, using the presented methods, it is difficult to control the size of the resulting particles and create island-type catalysts, which are important factors in the synthesis of the most efficient and optimized catalysts.

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