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## Catalysts for selective hydrogenation of aromatic nitrocompounds and hydrocarbons

**Abstract:** The liquid-phase hydrogenation of nitrocompounds and aromatic hydrocarbons at the elevated pressure of hydrogen on the mono- and bimetallic supported catalysts was studied. The optimum technological parameters of reactions for obtaining a high yield of target products were determined. It was shown that the mechanism of transforming aromatic nitro compounds – hydrogenation and it was identical for all solvents. It was studied the influence of the added hydrogenation reaction product (p-aminophenol) during p-nitrophenol hydrogenation for determination the cause of reducing of velocity of hydrogenation. It was revealed that the monometallic Rh/Al<sub>2</sub>O<sub>3</sub> or bimetallic catalysts of Rh-Pt/Al<sub>2</sub>O<sub>3</sub> composite are the most active catalysts for hydrogenation of aromatic hydrocarbons. The catalysts applied on aluminum oxide are more active and selective, than the catalysts applied on a silica gel.

**Key words:** catalyst, hydrogenation, aromatic nitrocompounds, aromatic hydrocarbons.

### Introduction

Aromatic mono- and polyamines are applied in the synthetic dyes production for wools, clothes, furs and synthetic fibres (aniline, nitroaniline, phenylendiamines, aminophenols). Liquid-phase catalytic reduction of nitrocompounds for producing amines allows to carry out process at rather low temperatures that leads to the considerable decrease in expenses of the electric power and potential of explosion of system [1, 2]. At application different solvents the reaction performs in milder conditions, than at a steam method. Such method of amines synthesis is more pollution-free and amines are obtained with rather high yields [3, 4]. Processes of hydrogenation of aromatic hydrocarbons are one of important among large-tonnage processes of oil processing and organic chemistry [5], for example, from synthesizable benzene worldwide about 20% are applied further for cyclohexane producing. Process of catalytic hydrogenation of aromatic hydrocarbons gives the possibility not only to change the chemical structure of hydrocarbons in the important direction and to reach the high yields of target products but also to improve production characteristics of oil fuels, oils and raw materials for petrochemical processing [6-8]. It is well known that the processes of reduction of nitrocompounds and aromatic hydrocarbons are very

difficult and multistage. These reactions require careful selection of active, selective and enough stable catalysts, and also process conditions: solvent, temperature and hydrogen pressure. Thus the development catalysts for selective hydrogenation of aromatic nitrocompounds (on nitrogroup or a benzene ring) and aromatic hydrocarbons is a very important and perspective problem.

The purpose of work was a creation of the put (supported) catalysts on the basis of platinum metals; studying their activity in reactions of hydrogenation of nitrogroup in nitrocompounds, and also at hydrogenation of aromatic hydrocarbons (benzene, ethylbenzene, toluene, cumene) at elevated hydrogen pressure.

### Materials and Methods

*The equipment, applied reagents, compounds analysis*

In the work the put (supported) mono – and bimetallic catalysts on the basis of platinum metals and on the basis of Pd and Pt with the modifying additive – Cu were prepared. Content of the active metals was varied within 0.5-5.0 wt.%. For synthesis of catalysts PdCl<sub>2</sub> salts of «pure» brand and RhCl<sub>3</sub>·3H<sub>2</sub>O, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, RuOHCl<sub>3</sub>, CuSO<sub>4</sub>·5H<sub>2</sub>O salts of «chemically pure» brand were applied. Chro-

matographically pure nitrobenzol (NB), para-, ortho- nitrophenols (p-NP, o-NP), benzene (B), ethyl benzene (EB), toluene (T), cumene, which were prepared by vacuum distillation or a recrystallization, were used in this work. The physical and chemical properties of former to be hydrogenated compounds corresponded to references [9]. Reactions were carried out as with solvents (distilled water, alcohols C<sub>2</sub>-C<sub>5</sub> of «chemically pure» brand) as without solvents. Hydrogenation was researched with using of the electrolytic hydrogen from cylinder (99.8%) and for gas-liquid chromatography (GLC) helium from a cylinder (99.992%) was applied. For carrying out of the experiments on a liquid-phase hydrogenation the kinetic installation of high pressure (KIHP) consisting of the advanced autoclave of Vishnevsky with intensive hashing and a measuring part was used. The main part of KIHP – the advanced autoclave of Vishnevsky from a titanium of VT-3 (total amount – 60.0 ml) with the hermetic electric drive, turbine stirrer (rotation speed – 2.800 rev./min, stirring intensity – 40.000 Re). The experiments were carried out in the isobaric-isothermal mode by a method developed by authors of this article in a laboratory [10-12]. For the analysis of initial compounds and reaction products the methods of gas-liquid chromatography (GLC), diazometric titration and IR-analysis were used [13, 14]. In the work physical and chemical research techniques of catalysts: X-ray diffraction, IR-analysis method on «Specord JR-75» and «UR-20» were also applied. The synthesized catalysts were investigated by techniques a electron microscopy (scanning and penetration), BET, porosimetry, BET (by nitrogen adsorption on the apparatus «Accusorb»), porosimetry.

#### *Preparation of catalysts*

The catalysts for the hydrogenation of gasoline fractions were synthesized by impregnating a carrier (alumina  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, silica-SiO<sub>2</sub>, activated carbon) with aqueous solutions of the active metal salts. Before-hand carriers were crushed to fractions 0.1 and 0.2 of mm, washed out by distilled water at 80°C and dried at 100°C. For carrying out a stage of impregnation was prepared aqueous 1.0% solution with the compound containing the active component. Two-component catalysts (based on Pd-Pt, Rh-Pt, Pd-Rh) were prepared by joint impregnation of the carrier solutions of the corresponding compounds. Some samples of catalysts were reduced in hydrogen current at 200°C in the quartz furnace. If in the reduction time of the catalysts samples even slight quantities of HCl were noticed, the procedure of washing of the catalyst from Cl-1 ions was repeated. The prepared

catalysts were cooled to room temperature and stored in sealed containers in desiccators. Before each experiment, the catalysts in the conditions required for the experiment, in a solvent medium was reduced in hydrogen for 30 min.

## **Results and Discussion**

### *Reduction of nitrogroup in aromatic nitrocompounds*

Reduction of aromatic nitrocompounds has begun with selection of solvent. Among the solvents used in work (distilled water, C<sub>2</sub>-C<sub>5</sub> alcohols) isopropanol is the most suitable for hydrogenation of NP on Pd-catalyst, and on Pd-Pt, Pd-Cu – catalysts – ethanol. These solvents were also used for studying the process of hydrogenation under various pressure and temperatures. The products analysis during reaction showed that the mechanism of transformation of aromatic nitrocompounds is identical to all solvents and it is a hydrogenation mechanism. There were the least yields of arylamines when using distilled water and C<sub>4</sub>-C<sub>5</sub> alcohols for reduction of nitrocompounds on Pd-Pt-catalysts. When using isopropanol for these catalysts the yield of target amines decreased due to the side reactions (reduction by a benzene ring). So, at hydrogenation of NB in the final sample, except aniline, already at 20-25°C there was a cyclohexylamine-hydrogenate of a benzene ring (4-6%) and at further increase in temperature the content of cyclohexylamine increased to 8-10%. At hydrogenation of NB and NP on the Pd-containing catalysts hydrogenation of only nitrogroups was noted, irrespective of solvents and the applied experimental conditions. Herewith the yield of aniline made 94-99%, p-phenylenediamine – 97-98%, p-aminophenol – 89-97% and o-aminophenol – 83-94%.

At research of NP reduction in comparison with NB in identical experimental conditions the reduction rate of NP is slower, than NB recovery rate. The form of kinetic curves at change of a structure of aromatic nitro compound practically does not change. Herewith the reaction rate, the yield of aminophenol (AP) for p-NP is significantly higher, than in a case of o-NP. The studied nitro compounds on decrease in initial rate of hydrogenation on the synthesized catalysts form a row: NB>p-NP>o-NP. Emergence of OH-group in a molecule of aromatic nitrocompound in p- and, especially, in o-position, reduces adsorption of nitro compound on the surface of the catalyst. Due to this the ratio of reaction components (hydrogen and nitrocompounds) on the catalyst surface is broken, the reaction rate

and AP yield are reduced. Relatively low speed of o-NP reduction, apparently, is associated with a manifestation of ortho-effect [15, 16]. The ortho-effect is a set of all types of the spatial and stereo-electronic interactions of close located substituent and reaction center of a molecule. The substituent creates space barriers which prevent approaching of reagent to the reaction center and its solvating in solvent. Due to violation of coplanarity to an aromatic core, the substituent or reactionary at ortho arrangement there is a stereoelectronic braking

of reaction. Ortho substituents are close enough to the reaction center that considerable vicinal effect could occur.

p-AP was added to the reaction medium in equivalent amount during p-nitrophenol hydrogenation for determination the cause of reducing of velocity of hydrogenation. Addition of the reaction product reduces the reduction rate and the amount of absorbed hydrogen (see Tab.). Possibly it was due to the blocking effect of the surface of the catalyst reaction product – p-AP.

**Table** – Investigation reduction of n-NP and p-NP (calculated on 400 cm<sup>3</sup> of hydrogen) in the mixture with n-AP in an equivalent amount at 0.5 MPa, T = 30°C, catalyst- Pd-Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.05 g)

| # | The volume of absorbed hydrogen from the gas phase, cm <sup>3</sup> | W, sm <sup>3</sup> /min. |           | The ratio of the adsorption coefficient $b_1/b_2$ |
|---|---|--------------------------|-----------|---|
|   |   | p-NP                     | p-NP+p-AP |   |
| 1 | 100   | 85.0                     | 20.0      | 0.23  |
| 2 | 150   | 72.0                     | 16.0      | 0.22  |
| 3 | 180   | 65.0                     | 13.5      | 0.21  |
| 4 | 250   | 56.0                     | 12.0      | 0.21  |
| 5 | 300   | 34.0                     | 7.7       | 0.22  |

Ratio  $b_1/b_2$  indicates stronger adsorption of n-AP compared to n-NP. p-NP has fewer opportunities for access to the catalyst surface, as a surface of the catalyst in the first seconds of the reaction occupied by molecules of p-AP, which are readily adsorbed on the catalyst surface. Speed reaction hydrogenating the n-NP sharply reduced in the presence of p-AP, as catalyst surface poisoned by the reaction product. The calculation of the rate constants based on adsorption coefficients shows that the reaction rate constant, confirming the assumption of zero orders the reduction of p-NP on the substrate.

The data, which is obtained in this work, suggests reduction mechanism of investigated nitrocompounds. In the hydrogenation of o- and p-NP, apparently, at first is formed corresponding hydroxylamine derivative which is immediately rearranged into quinoneimine. For this reason, it is difficult to register particle by gas-liquid chromatography. Then quinoid group quite easily rearranges to the corresponding aminophenol. This reaction is substantially easier than the transformation of NO<sub>2</sub>-group into NH<sub>2</sub>-group.

#### *Hydrogenation of aromatics*

It was revealed that the most active catalysts in the hydrogenation of aromatics – monometallic Rh/Al<sub>2</sub>O<sub>3</sub> (%Rh – 4-5% wt.) or bimetallic – Rh-Pt/Al<sub>2</sub>O<sub>3</sub>

(atomic ratio of active metal – 3:7, 2:8, 1:9, total % – the content of metals: 5%). It is not required increase in temperature at hydrogenation of benzene in the absence of solvent; the process was carried out at 2.8-3.0 MPa. Hydrogenation of EB was carried out at heating the reaction system (not higher 50°C), and at room temperature – 20-25°C, with hydrogen pressures – 3.0-3.3 MPa.

It is revealed, that the hydrogenation of cumene was carried out only at elevated temperatures (50 to 70-80 °C) and hydrogen pressure – 3.2-3.3 MPa.

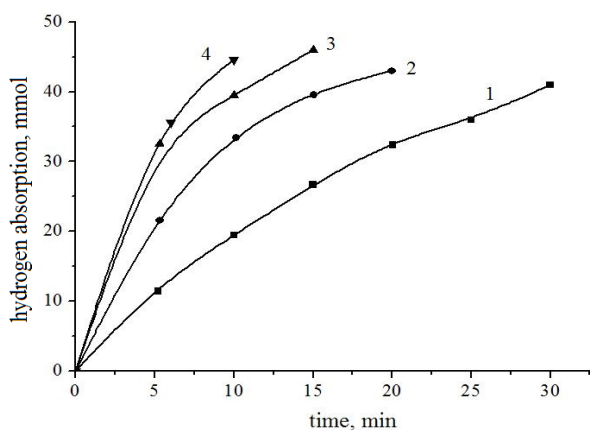
The reaction rate and the catalyst activity decreases in the series of catalysts: Rh-Pt>Rh-Pd>>Pd-Ru>Rh (fig.1). Bimetallic catalysts are more active and selective than monometallic. The maximum values of benzene and toluene conversion (85.0-93.0%) and yield of the corresponding hydrogenation products of the aromatic ring were found on the bimetallic catalysts Pd-Pt/Al<sub>2</sub>O<sub>3</sub> and Rh-Pt/Al<sub>2</sub>O<sub>3</sub>. Catalysts supported on alumina were more active and selective than the catalysts supported on silica. It was found that the reaction rate decreases with increasing complexity of the structure of compounds in the series: benzene>>ethylbenzene>cumene. These data are consistent with published data. Thus, according to [18-20], the rate of hydrogenation of benzene is higher than the rate of its homologues hydrogenation.

This is probably due to the presence of unsaturated side chains in aromatic hydrocarbons. GLC analysis and IR spectroscopy data showed the high yields of the desired products (up to 98-99%).

Hydrogenation of aromatic hydrocarbons on Pd-Pt-catalysts on various carriers was carried out. On catalysts supported on zeolites, in the reaction products the cracking products were also present in minor amounts (to 5.0%). There is a partial reduction of benzene to cyclohexene (10-18%) on Ru catalysts, the yield of cyclohexane – not higher than 30-46%. Optimum catalysts for the hydrogenation of benzene and toluene – the catalysts with ratio Pt:Pd = 3-7; 2-8; 1-9.

#### *Physico-chemical properties of the synthesized catalysts*

Specific surface area of the developed catalysts on the basis of various platinum metals is within values 175.0-290.0 m<sup>2</sup>/g. Addition of the second metal slightly reduces the specific area. The synthesized catalysts possess a developed surface and have high volume of pores. The volume of the pores of catalysts represents: Pt-Pd(1:1)/Al<sub>2</sub>O<sub>3</sub> S<sub>w</sub>=318.33 ml/g; Rh-Pd(1:1)/Al<sub>2</sub>O<sub>3</sub> – S<sub>w</sub>=282.25 ml/g; Rh-Pt(9:1)/Al<sub>2</sub>O<sub>3</sub> S<sub>w</sub>=313.28 ml/g; Rh-Pd(9:1)/Al<sub>2</sub>O<sub>3</sub> – S<sub>w</sub>=213.39 ml/g; Pd-Ru(1:1)/Al<sub>2</sub>O<sub>3</sub> – S<sub>w</sub>=297.09 ml/g.

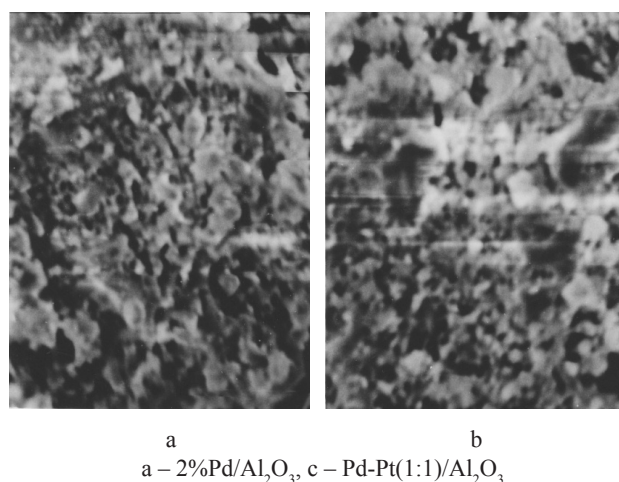


1-Rh, 2-Rh-Pd (1:1), 3-Rh-Pd(9:1), 4-Rh-Pt

**Figure 1** – The hydrogenation of benzene in an autoclave without solvent at different catalysts supported on Al<sub>2</sub>O<sub>3</sub>, P<sub>H<sub>2</sub></sub>=2.5 MPa, T=120°C

The used carriers and catalysts deposited on them were investigated by Scanning Electron Microscopy (SEM). Applying metals as mono- Pd/Al<sub>2</sub>O<sub>3</sub> (fig.2 a), and as bimetallic forms (in fig. 2b) produces a spe-

cific structure on the surface carrier. It was found that structure of Al<sub>2</sub>O<sub>3</sub> carrier consists of acicular crystalline structures. The initial sample of HZSM-5 is resented by predominantly extensive congestions of dispersible particles, which are located on the support surface. The dispersed particle size of ~ 5.0 nm occupies the large swathes of the carrier surface.



**Figure 2** – SEM-images

Microdiffraction patterns of catalyst with Pd/Al<sub>2</sub>O<sub>3</sub> composition corresponds to metallic Pd, moreover, there are in a small amount (4-5%) the particles of PdO. X-ray phase analysis of the catalyst of composition Pd/Al<sub>2</sub>O<sub>3</sub> showed the presence of the metallic phase Pd peak – ICDD No.87-0653, d = 2.25, 1.95, 1.38, and phase γ-Al<sub>2</sub>O<sub>3</sub> (2u = 458 d -1.99, 2u = 36.18 d-2.46) [21]. It was revealed the formation of solid solutions and the presence of traces of free Pd for systems Pd-Pt-catalyst. X-ray analysis of the reduced mixed Pd-Pt-catalysts showed that palladium indicated distinct midline intensity on the diffraction patterns; parameter of lattice didn't differ from the known in the literature. There are lines of Pd and unreduced oxide PdO on the diffractogram, and its amount is close to 10%. The results of temperature-programmed reduction (TPR) show that all Pd-containing catalysts possibly contain palladium in at least in two forms: PdO particles and Pd oxide species stabilized on a surface.

For studying the behavior of NP at hydrogenation in the liquid phase at hydrogen pressure it was synthesized supported catalysts based on Pd and Pt with builder – Cu. In the preparation of catalysts as the carriers were used γ-Al<sub>2</sub>O<sub>3</sub> and activated carbon (C). As a result of physico-chemical studies of catalysts it



was found that catalysts supported on a surface area C is almost 2 times greater than the surface of catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Pores of catalysts with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier have the shape of cylinders, which radius are within the range 20-22 Å. According to XPS, palladium on C is fully reduced to the zero-valent state, whereas  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, palladium is not fully reduced. Electron binding energy Pd<sup>0</sup> 3d<sub>5/2</sub> Pd/C is 336.5 eV, corresponding to Pd<sup>2+</sup>. Modification of the catalyst with copper ions does not change the binding energy of the electron Pd 3d<sub>5/2</sub>. By XRP-method was revealed that in the copper-modified catalysts based on Pd (Pd-Cu) – Pd is in the zero valence state, and the state of copper Cu is characterized by the binding energy of 2p<sub>3/2</sub> electrons, equals to 932.7 eV, corresponding to Cu<sup>+</sup>, so it's possible to suggest that Cu catalysts are in the form of Cu<sub>2</sub>O. It is found that in addition to the zero valent Pd, there is also oxidized form of palladium (PdO<sub>2</sub>) on the surface.

### Conclusion

The reactions of the liquid-phase hydrogenation of the nitro group in nitro compounds and the hydrogenation of aromatic hydrocarbons (benzene, ethylbenzene, toluene) at different temperatures and hydrogen pressures were studied. The effective selective catalysts on the basis of the platinum metals applied on various carriers were created. Chromatographic analysis showed that the conversion mechanism of aromatic nitro compounds is hydrogenated and it is identical to all solvents. The shape of the kinetic curves at changing the structure of aromatic nitro compounds are not virtually changed. The sharp decrease in the hydrogenation rate of aromatic nitrophenol, compared with nitrobenzene is probably associated with decrease in the adsorption capacity of o- and p-NP, especially in the case of o-NP. It is obvious that the presence of groups OH-substituents in the molecule in the case of NP reduces the rate of hydrogenation of the compounds. It was studied the influence of the added hydrogenation reaction product (p-aminophenol) during p-nitrophenol hydrogenation for determination the cause of reducing of velocity of hydrogenation. Addition of the reaction product reduces the reduction rate and the amount of absorbed hydrogen. Hydrogenation of aromatic hydrocarbons at elevated pressure of hydrogen was studied in the solvents and in the absence of solvents. Rh-Pt-catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are the most active catalysts in the process. The reaction rate and selectivity of the catalysts decreases in the series: Rh>Pt>Rh-Pd >>Pd-Ru>Rh.

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