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### Catalytic reduction of aromatic nitro compounds: general questions, equipment, enlarged laboratory tests

**Abstract:** The article is devoted to issues of amines production from nitro compounds. The processes of catalytic reduction of aromatic nitrocompounds by hydrogen to amines have practically superseded all other methods for the production of aromatic amines in large-tonnage plants. Aromatic mono-, di- and polyamines, due to their high reactivity, are widely used in the production of various compounds (photochemicals, fuel stabilizers and additives lubricating oils, in the paint and varnish industry, for painting natural and synthetic fibers). Authors compare methods of nitro compounds reduction and show different variants of apparatus design. The article also describes the results of enlarged laboratory examinations of the deposited catalysts synthesized by authors in reactions of p-phenylenediamine, p-amino-diethylaniline, o- and p-aminophenols production. By using relatively small amounts of catalysts (0.48-0.6 g of catalyst by hydrogenating 50 g of an aromatic nitro compound) were obtained high amine yields of 90-98.7%.

**Key words:** catalytic reduction, nitro compounds, amines, p-phenylenediamine, p-amino-diethylaniline, aminophenol.

#### Introduction

Aromatic nitro compounds are used mainly in the composition of explosives or as solvents. In general, these compounds are applied to reduce the aniline derivatives used in the production of paints, pigments, insecticides, textiles, plastics, resins, elastomers (polyurethane), pharmaceuticals, plant growth regulators, fuel additives and vulcanization accelerators for rubber and antioxidants [1]. The most important property of the nitro group is its ability to be reduced to an amino group. By this method aromatic amines are produced.

Aromatic mono-, di- and polyamines, due to their high reactivity, are widely used in the production of various compounds: synthetic dyes of various shades (for photography, in the paint and varnish industry, for painting natural and synthetic fibers), photochemicals, fuel stabilizers and additives lubricating oils, chemical plant protection products, synthetic fibers, sorbents, medicines, etc. [2-8]. Taking into account the extremely high volumes of commercial production of aniline and toluene diamines, the total

production of which in the world is more than 3-4 million tons/year, the problem of improving the technology of obtaining these compounds can be considered actual [9-13].

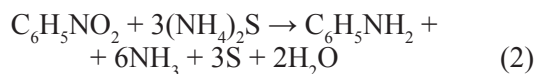
#### Aromatic nitro compounds reduction

The catalytic reduction of organic compounds, including aromatic mono- and polynitro compounds, to the corresponding amines is carried out in many variants, differing in the composition of the reaction masses, the aggregate state of the phases, the nature and type of the hydrogenation catalyst, the apparatus design of the process, the conditions of its conduct, etc. [14].

The reaction of aromatic nitro compounds reduction to amines by the action of ammonium sulphide on heating was discovered by N.N. Zinin in 1842 ("Zinin reaction") [15]. Zinin's reaction is a method of obtaining aromatic amines by reduction of nitro compounds (1):



Zinin acting on nitrobenzene with ammonium sulfide, obtained aniline (2):



Hydrogenation of aromatic nitro compounds can be implemented in the liquid or gas phase on the solid catalysts [16-18].

By the first option higher-boiling substances (dinitro-compounds, fats) are hydrogenated because their transfer to a gas form requires a large amount of hydrogen [19].

The second option is applied for the reduction of substances, the volatility of which at a reaction temperature is sufficient to create the necessary partial pressure of substances in the vapor mixture. By the second variant, for example, benzene, nitrobenzene, phenol can be hydrogenated [20, 22]. In all the variants heterogeneous catalysts are used. The most widespread catalysts are catalysts on the base of Group VIII metals and mixed catalysts.

In the case of a process in the vapor phase, copper is most often used on carriers, because the hydrogenation of the aromatic ring does not occur when using this catalyst.

In the papers [23-25] a catalytic method for the synthesis of aniline by hydrogenation of nitrobenzene in the vapor phase has been developed. Peculiarity of this method was mixing of aluminum hydroxide with a vanadium compound in the presence of water and nitric acid, then procedures of extruding, drying, calcination and then impregnation of the prepared mass with a solution of nickel and copper salts. In the work [26] a vapor-phase hydrogenation reaction of benzene on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with a small Ni content (up to 5 wt%) was carried out. In the works [27, 28] advantages and disadvantages of the vapor phase catalytic hydrogenation in industry are considered. Authors claimed that it is expedient to use modified heteropolycompounds for further improvement. They wrote that the film palladium catalysts may be the best for the selective reduction of acetylenic compounds to olefins. The authors have presented data on the selective hydrogenation of aromatics over these catalysts. In [29] authors offered to obtain aniline in the presence of a catalyst: Pd or Pt, supported on lipophilic carbon. The promoter is alkali metal hydroxide, carbonate or bicarbonate, Zn(OAc)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, at a temperature of 150-250°C. A method is also known for the production of aniline by hydrogenating nitrobenzene in the gas phase in the presence of a nickel-copper-vanadium catalyst [30].

In [31] the process for the preparation of a catalyst for the producing aromatic amines R-R<sub>1</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> (wherein R can be additionally NH<sub>2</sub>) is patented. By this method the desired product is obtained by hydrogenating the corresponding nitroaromatic hydrocarbons with hydrogen in the gas phase in the presence of a catalyst Pd (0.001-7% by wt of the catalyst) and Pb (0.1-50%) on graphite or graphite-containing coke as a substrate, which has a surface of 0.2-10 m<sup>2</sup>/g. Hydrogen is introduced in excess: 30-600 equivalents per equivalent of NO<sub>2</sub>-group.

The disadvantages of hydrogenation processes in the gas phase are:

- a high hydrogenation temperature (it contributes to the formation of a significant amount of by-products, a deterioration in the quality of the resulting catalyst and a decrease in the yield of the target products);
- a high pressure;
- the complexity of the process design of the reactions proceeding at high temperatures (which leads to a process cost increase, reactor designs and process diagrams);
- a relatively low catalyst load;
- the use of a large excess of hydrogen;
- a short inter-regenerative period of operation of the catalyst;
- a partial destruction of the catalyst;
- a partial loss of catalytic activity (and as a result of which the yield of aromatic amine products decreases);
- at high temperature of hydrogenation (up to 300-350°C) some nitro compounds can be decomposed, mono- and dinitro compounds in the mixture during evaporation can be converted into explosives;
- at high temperatures can be the aromatic ring hydrogenation;
- can be reactions of gumming and a deamination, which to a large extent deactivate the catalyst.

### The liquid-phase catalytic reduction of nitro compounds

The application of liquid-phase catalytic reduction of nitro compounds makes it possible to perform the reaction at sufficiently low temperatures, which leads to a significant reduction in energy costs and the explosion of the system.

In general, the reduction reactions of organic compounds can be divided into two groups:

1. The reduction by molecular hydrogen in the presence of hydrogenation catalysts;

2. The reduction with other inorganic and organic reagents is “a chemical” reduction.

### Nitro compounds reduction by molecular hydrogen

The most important way of amines producing from nitro compounds is catalytic reduction by hydrogen on catalysts. For the first time thanks to this method Zaitsev carried out such a reaction, passing over the platinum black nitrobenzene and hydrogen vapor. Later Sabatier implemented the such reaction over nickel and a number of other metals [32, 33]. A major contribution to the study of the catalytic reduction of nitro compounds was made by scientists from the USSR, the CIS, Russia and Kazakhstan [3, 4, 8-10, 12, 13, 22-25, 27, 28, 30, 32-42].

The reduction of nitro compounds can be carried out in the presence of both heterogeneous and homogeneous catalysts, but in the industry to date use only solid-phase heterogeneous catalysts [40, 43-46]. This is mainly due to the difficulty in isolating and regenerating the homogeneous catalyst for subsequent use.

### Laboratory equipment for the hydrogenation of aromatic nitro compounds

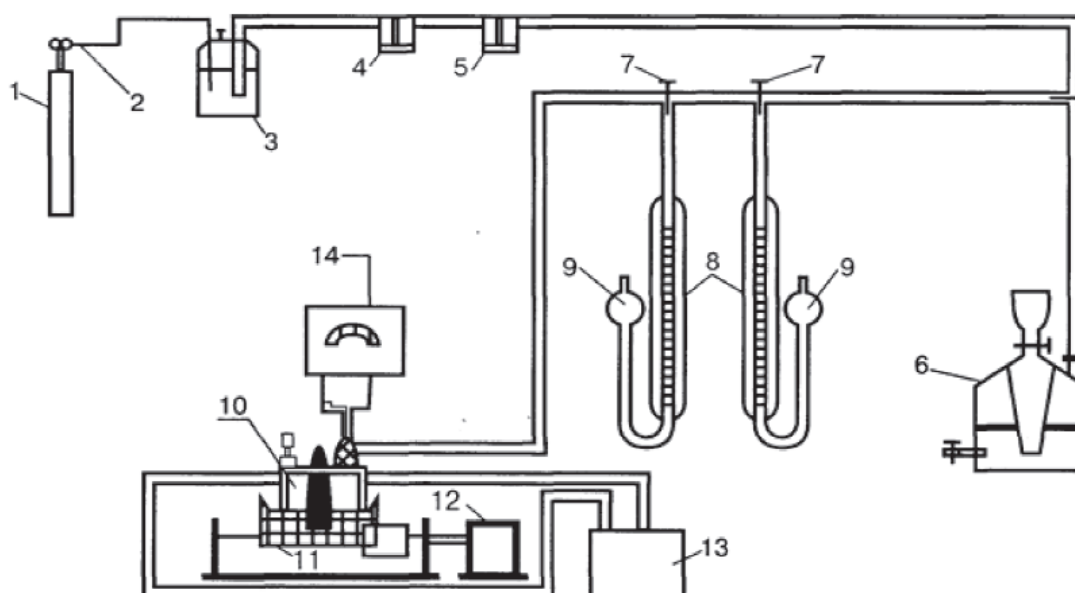
A widespread installation for hydrogenation of aromatic nitro compounds is installation on a basis

of “catalytic duck” (fig.1). Fig. 1, 2 show the installations with “a catalytic duck” for hydrogenation at atmosphere and elevated pressure.

Today hydrogenation at elevated and high pressures is widely used. The process is carried out in special apparatuses – high-pressure autoclaves, circulating apparatuses and other reactors.

Autoclaves are devices in which reactions under pressure are carried out. They come in two classes – low-pressure autoclaves designed for pressures up to 10 atm, and high pressure autoclaves up to 1000 at. The latter are more often used in chemical laboratories. Autoclaves are thick-walled metal vessels, often cylindrical or spherical. The autoclave is closed with a lid, the sealing is achieved by a shutter with the help of a cone seal or sealing rings made of non-ferrous metals (copper, aluminum, etc.) or plastics (rubber, asbestos, etc.).

High-pressure autoclaves were first widely applied by Ipatiev, whose work in this area dates back to 1903 (fig. 3). The Ipatyev autoclave (or bomb) is a forged cylinder with a flange head that joins the autoclave body with the help of the Ipatyev shutter. Mixing of the contents is achieved by tilting the autoclave and its slow rotation. Such an autoclave is very convenient to handle. It is easy to wash. An example of using such a device may be the process of hydrogenation of benzene to cyclohexane [49].



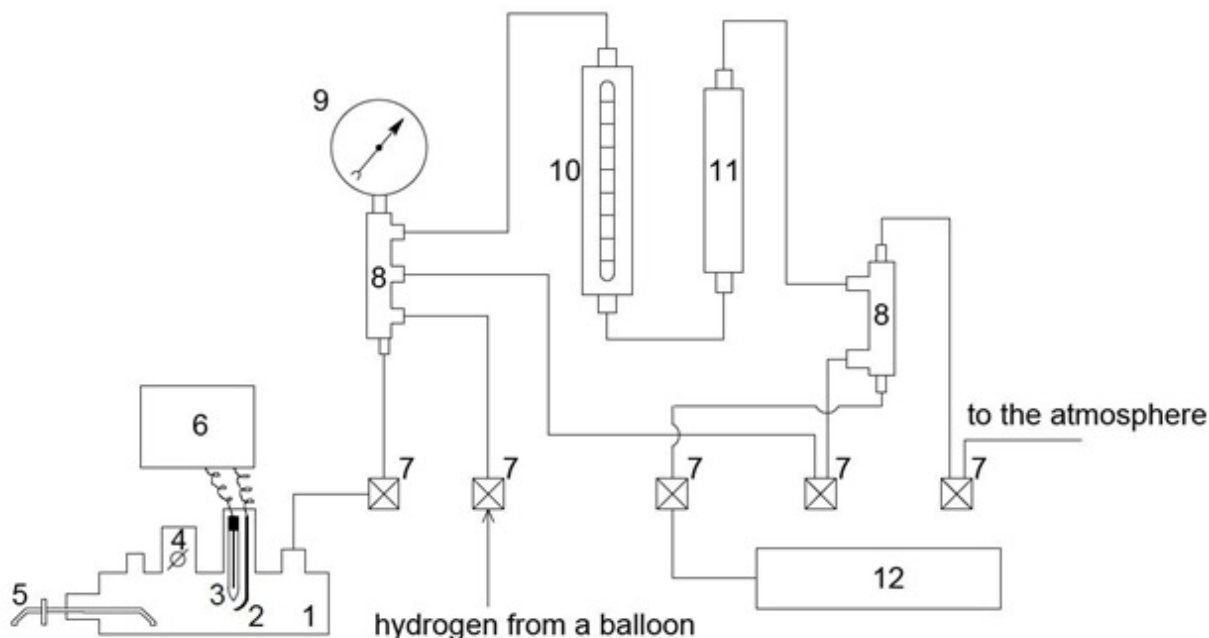
**Figure 1** – Scheme of the unit for the catalytic hydrogenation of aromatic nitro compounds:

1 – hydrogen generator; 2, 7 – the crane; 3, 4, 5 – cleaning bottles; 6 – gas meter; 8 – measuring burettes; 9 – pear; 10 – catalytic “duck”; 11 – rocking chair; 12 – electric motor; 13 – thermostat; 14 – potentiometer

In general, the autoclave is a steel cylinder with a spherical bottom and a bolted spherical cover. The lid is provided with a valve for supplying hydrogen and descending the pressure (in separate designs, a valve for sampling from the gas and liq-

uid phases), a thermowell sleeve and a manometer. Desirably, the autoclave was made of acid resistant steel.

There are known different types of autoclaves: rotating, swinging, horizontal, vertical and column.



**Figure 2** – An installation for liquid-phase hydrogenation at elevated pressure on the basis of catalytic “duck”: 1 – high-pressure device “duck”, 2 – platinum electrode, 3 – chlorine silver reference electrode, 4 – feed opening, 5 – sampler, 6 – potentiometer, 7 – fine adjustment valves, 8 – combs, 9 – gauge manometer, 10 – measuring burette, 11 – equalizing capacity, 12 – buffer capacity [47, 48]

In an autoclave with a magnetic stirrer of the N.E. Vishnevsky’ system (fig. 4) an electric motor rotating the stirrer is placed in a high-pressure zone. The magnetic flux of the stator located on the outside rotates the rotor placed inside the autoclave housing made of non-magnetic chromium-nickel steel. The rotor is fitted tightly onto the agitator shaft and rotates it through the bearings at high speed. Such an autoclave with a propeller stirrer is operated at a pressure of up to 300 atm and temperatures up to 300°C with a stirring speed of up to 3,000 per minute. In the autoclave, the sample can be sampled during the reaction, for which there is a special fitting connected to the siphon tube. The autoclave is heated by an electric furnace. To regulate the temperature of the autoclave, there is a water jacket and a pocket for the thermocouple. Through a special fitting, the reagents are loaded, and there is a discharge opening at the bottom. This design allows the autoclave to be fixed permanently and to perform its loading and unloading without disassembly. The autoclave is closed with a

lid and sealed with special pins with nuts.

Flow systems are also used for the hydrogenation of aromatic nitrocompounds. Continuous flow reactions have advantages over periodic reactions in terms of productivity, heating and mixing efficiency, as well as safety and reproducibility; in addition, automatic and multistage reactions are possible. The amount of waste can be minimized by using continuous flow conditions using solvents, free reagents, which leads to environmentally sustainable chemistry [50, 51].

Continuous flow reactions using heterogeneous catalysts (continuous flow catalytic reactions) can be ideal reaction systems, since the desired products that are easily separated from the catalysts are obtained continuously [52-54]. The authors of papers [55-57] develop various continuous flow systems with immobilized catalysts: hydrogenation of aromatic nitrocompounds using new palladium catalysts based on polysilane. The flow installation used by the authors of these works (fig. 5) is effective for the synthesis of



a number of nitrogen-containing compounds, which are key intermediates of many biologically active compounds and functional materials [58, 59]. The selective reduction of the nitro group proceeded quantitatively in the case of carbonyl compounds, such as esters and ketones. It is interesting to note that the ketone part was tolerant under the reaction conditions. Dinitro compounds can also be used in this flow-through reaction without inhibiting the product. The reduction of 2-nitroanisole was carried out quantitatively to obtain 2-aminoanisole under pure conditions without deactivating the catalyst. It is noted that the leaching of palladium was not observed in any of the reactions.

### Enlarged laboratory tests

For enlarged laboratory examinations we used installation on the basis of “catalytic duck” (fig.1, 2) and a high-pressure kinetic unit (HPKU), consisting of an advanced Vishnevsky autoclave with intensive mixing and a measuring part (fig.6). This installation is one of the most widely used in the hydrogenation of various compounds. The main part of the HPKU is an autoclave (fig. 4). The efficiency of the catalysts was calculated by the amount of hydrogen absorbed per unit time (60 seconds). During the reaction, samples are taken – after reaching the absorption of 1, 2 and 3 moles of hydrogen – for analysis of the hydrogenation products. The autoclave device allows to take samples for analysis without disturbing the equilibrium conditions of the experiment.

After the end of the reaction (as indicated by the stopping of hydrogen absorption), stirring is turned off and the hydrogen pressure is released to the atmosphere, and the catalyst is filtered off from the catalyst and the final analysis is carried out. In some cases, the final product is isolated to determine the % yield of the amine from the theoretically calculated reaction amount. To do this, after separating the catalyst filter, the solvent is evaporated, then the remaining material is washed on the filter with distilled water and dried at 40-50°C.

Chromatographically pure, prepared by distillation in vacuum or by recrystallization nitrobenzene (NB), ortho, para-, ortho-nitrophenols (o-NP, p-NP, o-NP), ortho, meta-, para-nitroanilines (o-NA, m-NA, p-NA) and p-nitrodiethyl aniline (p-NDA) were hydrogenated. Physicochemical parameters of the starting compounds corresponded to the reference. Distilled water, C<sub>1</sub>-C<sub>5</sub> alcohols of the grade “CP” were used as solvents.

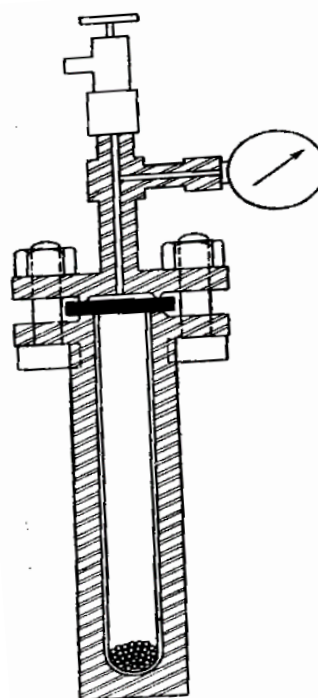


Figure 3 – Ipatiev' autoclave

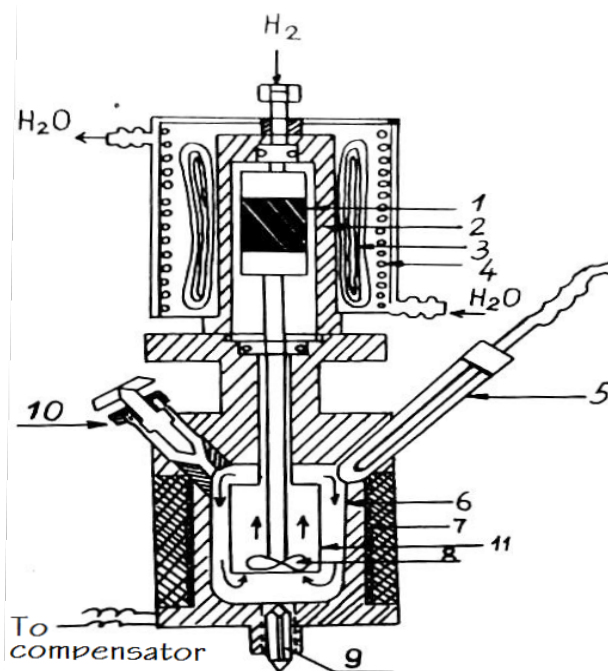


Figure 4 – The improved autoclave Vishnevsky with hermetic electric drive: 1 – rotor, 2 – a shielding sleeve, 3 – stator, 4 – cooling of the stator, 5 – thermocouple, 6 – reactor vessel, 7 – electrical heating, 8 – spiral mixer, 9 – lower cone valve, 10 – unit for enter the catalyst, the solvent and hydrogenated compounds, 11 – guiding glass

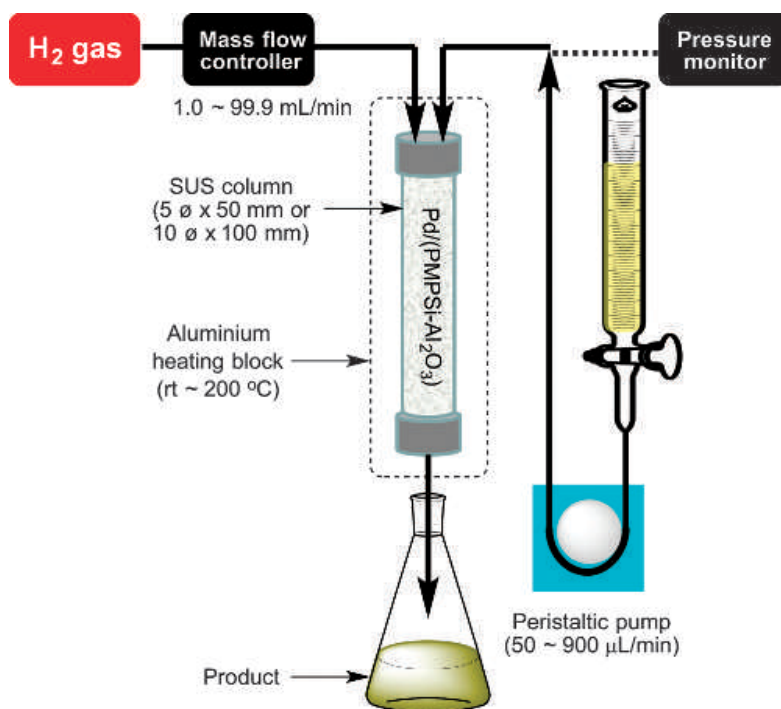


Figure 5 – Continuous-flow reactor

The reaction was carried out with electrolytic hydrogen from a balloon (99.8%), for gas-liquid chromatography (GLC), helium (99.992%) was used from a balloon.

For the calculations, the reaction rates for the first points and for the moment of absorption of

$1\text{MH}_2$  (or  $2\text{MH}_2$ , or  $4\text{MH}_2$ , depending of a reaction) are taken.

The selectivity of the process is calculated by the formula:

$$S_m = \frac{\text{The yield of the primary amine} \cdot 100\%}{\text{The yield of the primary amine} + \text{Yield of by-products}}$$

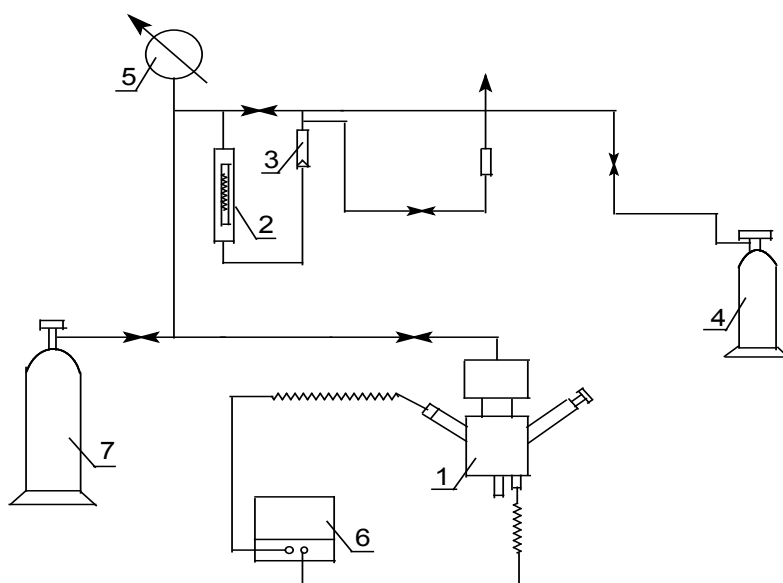


Figure 6 – High-Pressure Kinetic Unit: 1 – an autoclave of Vishnevsky; 2 – measuring burette; 3 – leveling capacity; 4 – buffer tank; 5 – gauge manometer; 6 – a device for determining and maintaining the temperature in the system; 7 – cylinder with hydrogen

For laboratory tests, catalysts deposited on  $\gamma\text{-Al}_2\text{O}_3$ , coal (C) of various grades,  $\text{CaCO}_3$  (shell) catalysts based on Pt and Pd, were prepared by applying appropriate compounds to the carrier by impregnation. To prevent hydrolysis using  $\text{PdCl}_2$ , a solution of NaCl was added to the solution. In the synthesis of Pd-Pt catalysts, 2% solution of  $\text{Na}_2\text{CO}_3$  was used in some cases.

Qualitative and quantitative analysis of the initial compounds and reaction products was carried out by TLC, GLC, diazometric titration, voltammetric titration, and oscillographic polarography [60-64]. An IR spectroscopic analysis was used. Physicochemical methods of studying catalysts (BET, electron microscopy) were also applied in the work.

## Results and Discussion

As a result of the hydrogenation of p-NDA in a catalytic “duck”, it was found that the change in the

mass of the sample of p-NDA does not affect the reaction rate, the initial reaction rate does not depend on the amount of hydrogenated material, i.e. the reaction order for the substance is zero. The activity of the Pd catalysts deposited on C is higher than for the samples of catalysts deposited on  $\text{Al}_2\text{O}_3$ , which agrees with a decrease in the basicity of the carrier, which affects the degree of electron interaction of the metal-carrier. By reducing the activity, the prepared catalysts are arranged in a row:  $\text{Pd} / \text{C} > \text{Pd} / \text{CaCO}_3 > \text{Pd} / \gamma\text{-Al}_2\text{O}_3$ .

The high catalytic activity of Pd-based catalysts compared to the Ni catalyst allowed the reaction to be carried out under milder conditions. Enlarged tests of p-NDA in an autoclave were carried out on 2% Pd/C in methanol at hydrogen pressures of 0.5-3.0 MPa (tab.1).

For hydrogenation of NB, p-NP, o-NP, m-NA, p-NA an autoclave with a total volume of 400 ml was used. For the charge, 50 g of the substance and 200 ml of solvent were taken (tab.2).

**Table 1** – Enlarged tests of p-NDA hydrogenation (31.5 g) in methanol p-ADA – para-amino-diethylaniline

T, K	$P_{\text{H}_2}$ , MPa	Amount of acatalyst, $q_{\text{cat}}$ , g	Yield of amine, p-ADA, %*	Duration of reaction, min.
2%Pd/C				
358	2.5	0.2	86.0	18.0
358	2.5	0.15	84.0	12.0
360	2.8	0.15	90.0	14.0
360	3.0	0.2	91.0	14.5
363	3.0	0.15	91.2	14.0
368	2.8	0.2	92.0	14.0
368	2.8	0.15	92.1	13.5
industrial Ni-Raney				
358-372	2.5-3.0	1.0-1.2	83.5-84.1	35.0- 45.0

\*- result of 5 parallel experiments

**Table 2** – Enlarged laboratory tests of NP and NA AP- Aminophenol, PhDA – Phenylenediamine

#	The starting compound, the resulting product (catalyst)	Yield, g*(%)	Amount of acatalyst, g	The temperature of the experiment, °C	Pressure of hydrogen, MPa	Duration of the test, min.
1	p-NP, p-AP (Pd/g)	114.0 (97,5%)	0,6	50-70	1.0-4.0	12-40
2	p-NP, p-AP (Pd-Pt/C)	105.1 (90%)	0.48	30-60	2.0-3.0	10-34

Continuation of table 2

#	The starting compound, the resulting product (catalyst)	Yield, g*(%)	Amount of acatalyst, g	The temperature of the experiment, °C	Pressure of hydrogen, MPa	Duration of the test, min.
3	p-NP, p-AP (Pd/g)	116.9 (98.5%)	0.55	50-70	1.0-4.0	14-38
4	o-NP, o-AP (Pd/g)	112.0 (96%)	0.6	50-70	1.0-4.0	30-44
5	o-NP, o-AP (Pd-Cu/g)	116.0 (98%)	0.6	50-70	4.0-5.0	35-52
6	p-NA, p- PhDA (Pd/g)	110.8 (95.2)	0.5	30-60	2.0-3.0	10-29
7	p-NA, p- PhDA (Pd-Pt/g)	115.0 (98.7%)	0.5	50-70	1.0-4.0	12-22

\*- Yield (g) – the sum of 3 parallel experiments

## Conclusion

The article summarized general issues of aromatic amine production from the corresponding nitro compounds. The authors described also own laboratory researches. The results of enlarged tests show that using relatively small amounts of catalysts (0.48-0.6 g of catalyst by hydrogenating 50 g of an aromatic nitro compound) it is possible to obtain high amine yields of 90-98.7%. The process time on bimetallic catalysts at hydrogenation of substances under identical conditions was lower than in the case of using only a monometallic Pd-containing catalyst. When comparing hydrogenation of the big batches of compounds the authors found that the reduction process p-NA is faster than for p-NP and, especially, for o-NP. It was also noted that 5-7% o-aminocyclohexanol appeared in the product samples. For this reason, the yield of the target product – p-AP was lower than expected (90%).

## References

1. <http://chem21.info/info/667763/>
2. Charushin V.N. *Sorovsky educational journal*. 2000. – Volume 6, No. 3. – Pages 64-72.
3. Sassykova L.R., Masenova A.T., Bizhanov F.B. *Inst. org. Katal Elektrokim*, 1995, 3, 21-26.
4. Sassykova L.R. Catalytic reduction of aromatic mono- and dinitrocompounds. Diss...chem. sci. // Kazakhstan, Almaty, 1996, 223 p.
5. Rafiq K.A., Mohammad K.K., Shahnaz P.J. *Pharm. and Biomed. Anal.* 2002. Vol. 29, № 4. – P. 723-727.
6. Abdullaev M.G., Klyuev M.V. *Pharm. Chem. J* – 2005. Vol. 39, № 12. – P. 655-657.
7. Jurgen H. (ed) *Encyclopedia of Industrial Chemistry, Ullmann's, Wiley*, Florida, 1985.
8. Aubakirov Y.A. Development of methods for the catalytic synthesis of industrially important amino products. Author's abstract. diss... cand. chem. sciences, Kazakhstan, Almaty, 1996, 27 p.
9. Kozlov A.I., Zbarsky V.L. *Russ. Chem J.* – 2006. – V.L, No. 4. – Page 131.
10. Sokolsky D.V. Hydrogenation in solutions. Alma-Ata: Publishing House of the Academy of Sciences of Kaz. SSR. 1962. 457 p.
11. Ashmore P. *Catalysis and inhibition of chemical reactions*. Translation from English A.A. Slinkin, Moscow: The World, 1966. – P. 151-237.
12. Shmonina V.P. in: Catalytic reduction and hydrogenation in the liquid phase. – Ivanovo, 1970. – P. 8-17.
13. Sassykova L.R. Theory and technology of catalytic petrochemical productions. – Almaty, Qazaq University, 2018. – 296 P. ISBN 978-601-04-3249-9.
14. Berkman B.E. Industrial synthesis of aromatic nitro compounds and amines. – Moscow: Publishing house "Chemistry", 1964.
15. Zinin N.N. Works on organic chemistry. – M.: Science, 1982. – 262 p.



16. Zhilin V.F., Zbarsky V.L., Kozlov A.I. Reduction of aromatic nitro compounds, – M.: RCTU. Published. center, 2004. – 92p.
17. Gates B., Quetzir J., Schuit G. Chemistry of catalytic processes. – Translated from English. – M.: Mir, 1981. – 552 p.
18. Gildebrand E.I., Fasman A.B. Skeletal catalysts in organic chemistry. – Alma-Ata: Science, 1982. – 136 p.
19. Masters K. Homogeneous catalysis by the transitional metals. – Translated from English – M.: Mir, 1983. – 552 p.
20. Gankin V.Yu., *New general theory of a catalysis*. – L.: Chemistry, 1991. – 80 p.
21. Tanabe K. Catalysts and catalytic processes. – M.: Mir, 1993. – 176 p.
22. Patent 2083540 Russian Federation, C 07 B 31/00. Method for hydrogenation of organic compounds. Datsevich L.B., Mukhortov D.A.– publ.1997. – 6 pp.
23. Pat. 2207335 Russian Federation, C 7 C 211/48, 211/46, 209/36. A process for the preparation of aromatic amines by reduction of the corresponding nitro compounds. Vinokurov V.A., Stycenko V.D., Patapenkov S.A., publ. 2003. – 6 pp.
24. Patent 2102138 Russian Federation, 6 B 01 J 23/847, 37/04. Method for the preparation of catalyst for the synthesis of aniline. Kladova N.V., Borisova T.V., Korobko L.N., publ. 1998, Bull. No. 2. – 14 p.
25. Patent 2093262 Russian Federation, 6 B 01 J 23/847, 37/02, 37/04. Method for the preparation of catalyst for the synthesis of aniline. publ.1997, Bull. No. 29. – 10 p.
26. Land Y., Fan Z., Li Y., Tang D., Li Y., Coug Y., Guofang Kejialaxuexuebao = Y. Nat. Univ. Def. Technol. – 1997. – 19(3), p.109 – 113.
27. Novalikhina M.D., Krylov O.V. Journal of Kinetics and Catalysis. – 2001. – 42 (1). – P. 86 – 98.
28. Novalikhina M.D., Krylov O.V. Uspekhi Khimii. – 1998. – 67 (7) – pp. 656 – 683.
29. Pat. 5283365 USA. *A method for obtaining aniline of high purity. Process for preparing high-purity aniline* / Nagata Teruyuki, Kobayashi Takashi, Watanabe Katsuji, KonoYoshitsugu, Tamaki Akihiro; Mitsui Toatsu; publ. 1944.
30. Author's Certificate 302333 USSR, C 07 C 85/10, C 07 87/52. Method for the production of aniline / Tsatsko IM; publ. 28.04.71. Bul. № 15. – 2 p.
31. Application 19521587 Germany, MKI6 S 07 C 211/45, B 01 J 23/62. Method and catalyst for the preparation of aromatic amines by hydrogenation in the gas phase. *Verfahren und Katalysator zur Herstellung von aromatischem Amin durch Gasphasenhydrierung* / Langer Reinhard, Buysch Hans – Josef, Pentling Ursula; publ. 19.12.96.
32. Fasman A.B., Sokolsky D.V. Structure and physico-chemical properties of skeleton catalysts. – Alma-Ata: Science of KazSSR, 1968. – P.115-140.
33. Nikolaev Yu.T., Yakubson A.M. Aniline, M.: Chemistry, 1984. 148 p.
34. Sokolsky D.V., Druz B.A. Introduction to the theory of heterogeneous catalysis. M.: High School. 1981. 216 p.
35. Sokolsky V.D. in: Hydrogenation catalysts. Alma-Ata: Science of KazSSR, 1975. pp. 7.
36. Sokolsky D.V. Hydrogenation in solutions. Alma-Ata: AN Kaz. SSR. 1962. 457 p.
37. Klyuev M.V. *Journal of Organic Chemistry*. 1987. Vol. 23. p. 581-585.
38. Tereshko L.V. Synthesis of aromatic and fatty aromatic amines on palladium-containing catalysts. Diss...chem. sciences. – Ivanovo, 1990, 163 p.
39. Kochetova L.B., Klyuev M.V., Petrochemistry. 1997. Vol.37. № 5. P.420-426.
40. Sokolsky D.V. in: *The mechanism of catalysis*, part 1. Novosibirsk. Science. 1984. p. 87-101.
41. Klyuev M.V., Vainstein E.F., *Proc. 6-th European Symp. on Organic reactivity*. Louvain-la-Neuve. 24-29 juli 1997. P. 143.
42. Klyuev M.V., *Russian polymer news*. 1998. V. 3. № 3. P. 27-29.
43. Pernoud L., Candy J.P., Didillon B., Jacquot R., Basset J.M. *Studies in Surface Science and Catalysis*. – 2000. – No 130. – P. 2057 – 2062.
44. Voronin M.V., Nasibulin A.A., Klyuev M.V. *Journal of Organic Chemistry*. 1997. Vol.33. №11. P. 1696-1698.
45. Johnstone R.A., Wilby A.H., Entwistle I.D. *Chemical Reviews*, **85(2)**, 1985, 129-170.
46. Masenova A.T., Sassykova L.R., Bizhanov F.B. “*Europacat-2*”, Netherlands, Maastricht, 1995.
47. Sassykova L.R., Otzhan U.N., Kurmansitova A.K., Serikkanov A.A., Aubakirov Y.A., Zhumakanova A.S., Kenzhebekov A.S. *News of ASRK, series of chemistry and technology*, 2017, 422 (2), 147-156.
48. Otzhan U.N., Kurmansitova A.K., Sassykova L.R., Serikkanov A.A., Kenzhebekov A.S., Starikov E.B. *Intern J of Biology and Chemistry*, 2016, 9(2), 40-44.
49. Wikipedia contributors. (2018, March 5). *Autoclave*. In Wikipedia, The Free Encyclopedia. Retrieved March 29, 2018, from <https://en.wikipedia.org/w/index.php?title=Autoclave&oldid=828918578>
50. Puglisi A., Benaglia M., Chiroli V. *Green Chemistry*, 2013, 15(7), 1790.

51. Rebrov E.V., Schouten J.C., Croon M. H.J.M. *Chemical Engineering Science*, 2011, 66 (7), 1374-1393.
52. Aijaz A., Xu Q., *Journal of Physical Chemistry Letters*, 2014, 5(8), 1400-1411.
53. Matsumoto T., Ueno M., Wang N., Kobayashi Sh., *Chemistry – An Asian Journal*, 2008, 3(2), 196-214.
54. Javaid R., Kawasaki Sh., Suzuki A., Suzuki T.M., *Beilstein Journal of Organic Chemistry*, 2013, 9, 1156-1163.
55. Masaharu Ueno, Yasuharu Morii, Kiyoko Uramoto, Hidekazu Oyamada, Yuichiro Mori, Shū Kobayashi, *Journal of Flow Chemistry*, 2014, 4(4), 160-163.
56. Naiwei Wang, Tsutomu Matsumoto, Masaharu Ueno, Hiroyuki Miyamura, Shū Kobayashi, *Angewandte Chemie International Edition*, 2009, 48(26), 4744-4746.
57. Juta Kobayashi, Yuichiro Mori, Shū Kobayashi, *Chemical Communications*, 2005, 20, 2567.
58. Tetsu Tsubogo, Yasuhiro Yamashita, Shū Kobayashi, *Topics in Catalysis*, 2014, 57(10-13), 935-939
59. Hidekazu Oyamada, Ryo Akiyama, Hiroyuki Hagio, Takeshi Naito, Sh. Kobayashi, *Chem. Comm.*, 2006, 41, 4297.
60. Sassykova L.R., Kasenova D.Sh., Masenova A.T., Bizhanov F.B., *Russ. J. Appl. Chem.*, 71, 1401-1403(1998).
61. Sassykova L.R., *Chemical and biochemical engineering quarterly*, 2017, 31(4), 447-453.
62. Heyrovsky M., *J. Electroanal. Chem.*, 1970, v. 28, №2, p. 409-420.
63. Sassykova L., Aubakirov Y., *Chiang Mai Journal of Science*, 45, 1, 2018, 474-483.
64. Stradyn J.P. **Polarography of organic nitro-compounds**, Riga, Acad Latv. SSR, 1961.