HYDROGENATION OF AROMATIC NITRO-COMPOUNDS OF A DIFFERENT STRUCTURE IN A LIQUID PHASE

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ABSTRACT

A comparative study of the kinetic regularities of the reduction of aromatic nitro-compounds of a various structure (nitrobenzene, nitrophenols, nitroanilines and p-nitrodiethyl aniline) on Pd and Pd-Pt catalysts deposited on various carries is carried out. Comparative hydrogenation of nitro compounds and nitrocompounds in a mixture with the corresponding amines (the reaction products) was studied. The presence of the hydrogenation products (amines) having a stronger propensity to adsorption on the catalyst surface than the starting hydrogenated compounds may cause decrease of the process speed and amount of absorbed hydrogen. The ratio of the adsorption coefficients confirmed it. It was revealed that at comparative hydrogenation of nitro compounds of various structure in ethanol and isopropanol the rate decrease upon transition from nitrobenzene to nitroanilines, p-nitrodiethyl aniline and nitrophenols. In this work target amines are obtained at low amounts of synthesized catalysts under mild conditions up to 89 - 99 %.

Keywords: aromatic nitro compounds, hydrogenation, nitroaniline, p-nitrodiethyl aniline, nitrophenol, supported catalysts.

INTRODUCTION

The high reactivity of aromatic nitro-compounds due to the presence of nitro groups in conjugation with the electronic system of the aromatic ring determines their wide application in the synthesis of a huge range of different compounds [1 - 7]. The synthesis of amines by hydrogenation of the corresponding nitro-compounds in the presence of catalysts is the most promising method [8 - 11]. One of the main problems of catalysis and theoretical organic chemistry refers to the clarification of the effect of the chemical structure of the hydrogenated substances on the reaction rate, for example, in case of introducing a functional group, hydrogen, sulfur, nitrogen or oxygen [12 - 14]. Since the chemical reaction is preceded by an adsorption stage in heterogeneous catalysis, a large number of discoveries in the field of the theory of catalysis is associated with the study of the structure of molecules and their adsorption on the surface of the catalyst. There is no doubt that there is a relationship between the structure of the adsorbed molecules and the coordination compounds and the chemistry of the transition metal complexes, which are the active components of the catalytic systems of the various reactions. The substituents in any organic molecule, and in this case - in the molecule of an aromatic nitro- compound,

have a significant effect on both the distribution of the electron density and the adsorption of the compound on the catalyst surface. The adsorption capacity of the nitro-compound can either decrease, or increase depending on the type of the substituent and which is why the ratio of the reagents on the catalyst surface changes [15, 16].

The reduction reaction of p-nitrodiethyl aniline (p-NDA) is of great practical importance, since the product of the reaction - p-aminodiethylaniline (p-ADA) (Fig. 1) after acidification with sulfuric acid (at 203 K and pH>3) is used in photo- and film industry for the processing of multi-layer photosensitive materials (Fig. 2). In industry, the hydrogenation of p-NDA is carried out under stringent conditions in methanol at skeletal nickel catalysts having pyrophoric; the reaction is characterized by a considerable duration and a high catalyst consumption. In the literature there are single sources on the hydrogenation of p-NDA, these studies are not systematic. So the implementation of the reduction reaction of p-NDA in the liquid phase in order to select a highly active non-pyrophoric catalyst and mild synthesis conditions of the corresponding amine is an actual issue.

The study of the kinetics and the mechanism of the processes of reduction of aromatic nitro-compounds in presence of the corresponding amines and the creation of highly efficient selective catalytic systems is one of the topical directions in the development of modern scientific technologies. In particular, in this work the research of the reduction of various nitro-compounds (nitroanilines, nitrophenols, nitrobenzene) on supported metal catalysts in a liquid phase under mild conditions is described. Methylphenylenediamine (a brown dye for wool), p-phenylenediamine (a black dye for wool) and aminophenols obtained as a result of the hydrogenation are valuable intermediates for the synthesis of film and photographic materials, dyes and medicines [17, 18]. Kazakhstan has no enterprises for the production of amine compounds. Therefore, the comparative study of the hydrogenation of nitroanilines and nitrophenols is relevant both from a theoretical and a practical point of view for Kazakhstan. The aim of the study was also to study the effect of the reaction product on the poisoning of the catalyst. For this, a comparative reduction of nitro compounds in a mixture with the corresponding amines (products of their reduction) was researched.

EXPERIMENTAL

Chromatographically pure nitrobenzene (NB), para-, ortho-nitrophenols (p-NP, o-NP), meta-nitroaniline (m-NA), para-nitroaniline (p-NA) and p-nitrodiethyl aniline (p-NDA) were prepared by distillation under vacuum or by recrystallization. Physicochemical parameters of the starting compounds corresponded to the reference data.
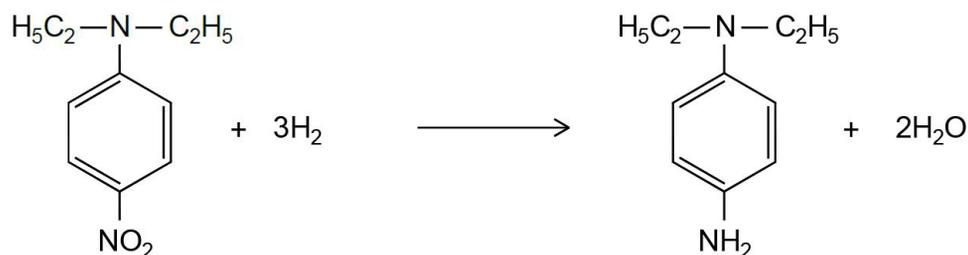
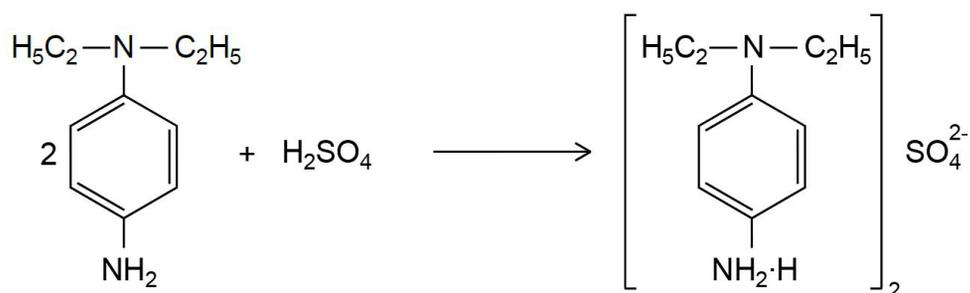Fig. 1. Hydrogenation of p-NDA to the corresponding amine.

Fig. 2. The interaction of p-NDA with sulfuric acid in order to obtain a valuable product for the photographic and film industry.
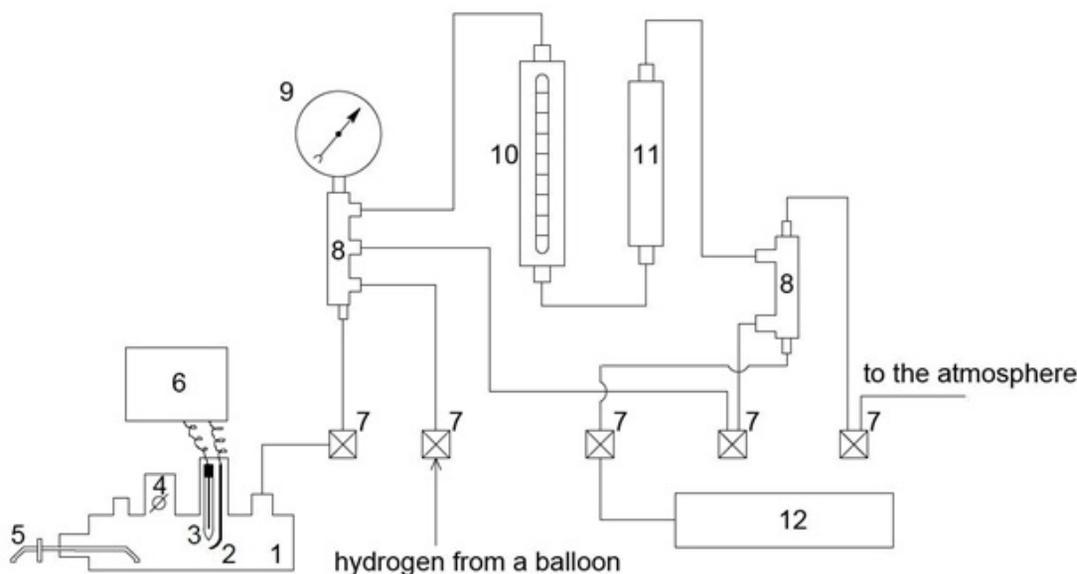
Fig. 3. Installation for liquid-phase hydrogenation at elevated pressure on the basis of catalytic "duck": 1 - high-pressure device "duck", 2 - platinum electrode, 3 - chlorine silver reference electrode, 4 - feed opening, 5 - sampler, 6 - potentiometer, 7 - fine adjustment valves, 8 - combs, 9 - gauge manometer, 10 - measuring burette, 11 - equalizing capacity, 12 - buffer capacity.

Distilled water and C_1-C_5 alcohols of a "chemical pure" grade were used as solvents. The reaction was carried out with electrolytic hydrogen from a balloon (99.8 %); helium (99.992 %) was used from a balloon for gas-liquid chromatography (GLC). Liquid phase hydrogenation of nitro compounds was studied at atmospheric pressure in the installation with the catalytic reactor "duck". The process under increased hydrogen pressure was carried out in a high pressure kinetic installation based on steel "duck" Kh18N9T (Fig. 3) and an improved Vishnevsky autoclave made of titanium [19 - 22].

The initial reaction rates and at those referring to 1M H_2 absorption were recorded.

The qualitative and quantitative analysis of the starting compounds and the reaction products was carried out by TLC, GLC, diazometric titration, voltammetric titration, oscillographic polarography [23 - 25]. IR spectroscopic analysis using Specord JR-75 and UR-20 was carried out. Physicochemical methods of studying the catalysts used (BET, electron microscopy, XRF) were also applied.

In this work, catalysts based on Pt and Pd deposited on γ-Al_2O_3, coal (C) of different grades, $CaCO_3$ (shell) were used. The catalysts were prepared by applying the appropriate compounds to the carrier by impregnation.

For prevention of hydrolysis (when using $PdCl_2$) NaCl solution was added to solution. At synthesis of Pd-Pt catalysts in certain cases 2 % Na_2CO_3 solution was applied.

RESULTS AND DISCUSSION

It was found by results of the hydrogenation of p-NDA in a catalytic "duck" 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 Pd-catalysts deposited on C is higher than that of the catalysts deposited on Al_2O_3, which is in agreement with the decrease of the carrier basicity affecting the degree of the metal-carrier electron interaction. The activity of the catalysts prepared follows the line: Pd/C > Pd/$CaCO_3$ > Pd/γ-Al_2O_3.

The high catalytic activity of Pd-based catalysts compared to Ni-catalyst allowed the reaction to be carried out under milder conditions.

The tests with increased p-NDA amounts are carried out in methanol in an autoclave using 2 % Pd/C at hydrogen pressure of 0.5 MPa - 3.0 MPa (Table 1). The large-scale tests showed the high efficiency of Pd-based catalysts compared to industrial Ni-Raney: an increase in

Table 1. Enlarged tests for hydrogenation of p-NDA (31.5 g) in methanol.

T, K	P_{H2}, MPa	$q_{catalyst}$, g	Amine yield, %*	Reaction duration, min
2 % Pd/C				
358	2.5	0.2	86	18.0
358	2.5	0.15	84	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

the yield of the target product, a shorter reaction duration, a reduction in catalyst costs.

The hydrogenation of the aromatic nitro-compounds (NB, NA, NP) studied proceeds in an autoclave with a wide variation of the process conditions. The most suitable solvents are found to be ethanol and iso-propanol. The shape of the kinetic curves of m-NA reduction shows a strong poisoning of a part of the catalyst surface by the reaction product. Experiments on the joint

Fig. 4. Kinetic curves for the reduction of p-NA and mixtures with p-PhDA in an equivalent amount in isopropanol at PH_2 = 1.0 MPa, T = 303 K, A_{3H2} = 800 cm³, q = 0.1 g.

hydrogenation of m-NA and the corresponding amine (m-phenylenediamine, m-PhDA) obtained as the reduction product (Fig. 4, Table 2) are carried out aiming to verify this assumption.

The amount of the absorbed hydrogen is considerably greater than that theoretically calculated in case of mixture reduction. Apparently, m-PhDA, being adsorbed on the surface of the catalyst gives no access of the hydrogen and the hydrogenated substance. The ratio of the adsorption coefficients shows also that m-PhDA has a stronger susceptibility to adsorption on the catalyst surface than the initial compound, i.e. m-NA. Thus, these studies support the assumption that the decrease of the process rate and the absorbed hydrogen amount can be attributed to the effect of the reaction product presence.

The effect of the reaction product, p-aminophenol (p-AP), introduced into the reaction medium in an equivalent amount, was also studied, as in the case of m-NA. When the product, p-AP, is added, the reaction rate and the amount of absorbed hydrogen are reduced (Table 3). This phenomenon is due to the blocking of the catalyst surface by the reaction product, p-aminophenol. In this case, as in the hydrogenation of m-NA in a mixture with m-PhDA, the ratio of b_1 and b_2 indicates a stronger adsorption of p-AP compared to that of p-NP. Probably,
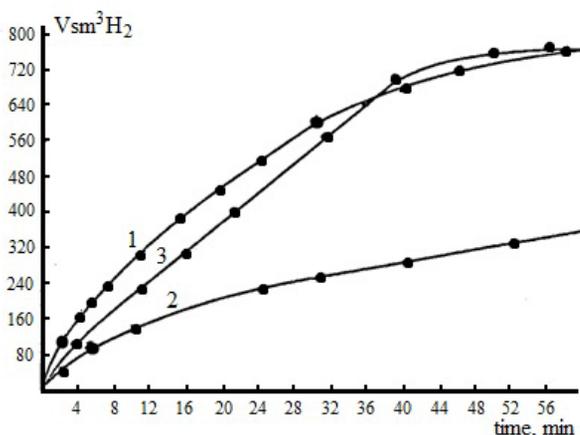
Table 2. Reduction of m-NA and m-NA in a mixture with m-PhDA (calculated on 800 cm^3 of hydrogen) in an equivalent amount at 1.0 MPa, T = 303 K, catalyst - Pd-Cu/γ-Al$_2$O$_3$ (0.05 g).

No	Volume of hydrogen absorbed from the gas phase, cm^3	Initial reaction rate W, cm^3/min.		The ratio of adsorption coefficients b$_1$/b$_2$
		m-NA	m-NA+m-PhDA	
1	50	75.0	25.0	0. 33
2	100	55.0	20.0	0.36
3	200	35.0	8.0	0. 23
4	300	28.0	7.5	0. 27
5	400	26.0	6.0	0. 23
6	600	20.0	4.0	0.20
7	700	17.0	3.0	0. 18

Table 3. Reduction of p-NP and p-NP (based on 400 cm^3 of hydrogen) in a mixture with p-AP in an equivalent amount at 0.5 MPa, T = 600ºC, catalyst - Pd-Cu /γ-Al$_2$O$_3$ (0.05 g).

No	Volume of hydrogen absorbed from the gas phase, cm^3	Initial reaction rate W, cm^3/min.		The ratio of adsorption coefficients 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

p-NP has less access to the surface of the catalyst, since it is already occupied by p-AP molecules within the first seconds of the reaction as they are quickly and easily adsorbed. The rate of the hydrogenation reaction of p-NP is significantly decreased in the presence of p-AP due to the poisoning of the catalyst surface by the reaction product. The magnitude of the rate constants, taking into account the adsorption coefficients, shows that the reaction rate is constant, and this verifies the assumption of a zero order of p-NP reduction on the substrate.

The data received in this work allow to assume the mechanism of reduction of the studied nitro compounds. In case of hydrogenation of o- and p-NP, the corresponding hydroxylamine derivative is presumably formed at the beginning. It turns immediately into quinoneimine. The latter is difficult to detect by GLC as the process takes place in a very short period of time. After this, the quinoid group is very quickly converted and the corre-

sponding aminophenol is obtained. The latter reaction proceeds much more easily than NO$_2$-group conversion to NH$_2$-group.

p-NA is probably reduced under the hydrogenation conditions studied in accordance with to the following scheme:

$$p\text{-NA} \xrightarrow[K_1 = 0.06]{2H_2} p\text{-aminohydroxylamine} \xrightarrow[K_2 = 0.17]{2H_2} p\text{-PhDA}$$
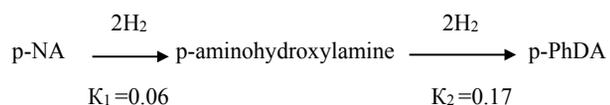
The hydrogenation of the nitro-compounds of a various structure proceeding in ethanol and isopropanol has a rate decreasing from NB to NA, p-NDA and NP. The line obtained is as follows: NB > p-NA > m-NA > p-NDA (p-NP) >> o-NP.

The significant decrease observed is probably due to a decrease in the adsorption capacity of o- and p-NP, most notably in case of o-NP. Probably, the presence of

Table 4. Results of enlarged laboratory tests of p-HA, o-NP, p-NP.

No	The hydrogenated nitro compound, the resulting product (catalyst)	Yield, g*(%)	Catalyst consumption, g	Experience temperature, K	Pressure of hydrogen, MPa	Duration of reaction, min
1	p-NP, p-AP (Pd/γ-Al$_2$O$_3$)	114.0 (97.5%)	0.6	323-343	1.0-4.0	12-40
2	p-NP, p-AP (Pd–Pt/C)	105.1 (90%)	0.48	303-333	2.0-3.0	10-34
3	p-NP, p-AP (Pd/γ-Al$_2$O$_3$)	116.9 (98.5%)	0.55	323-343	1.0-4.0	14-38
4	o-NP, o-AP (Pd/γ-Al$_2$O$_3$)	112.0 (96%)	0.6	323-343	1.0-4.0	30-44
5	o-NP, o-AP (Pd-Cu/γ-Al$_2$O$_3$)	116,0 (98%)	0.6	323-343	4.0-5.0	35-52
6	p-NA, p-PhDA (Pd/γ-Al$_2$O$_3$)	110.8 (95.2)	0.5	303-333	2.0-3.0	10-29
7	p-NA, p-PhDA (Pd–Pt/γ-Al$_2$O$_3$)	115.0 (98.7%)	0.5	323-343	1.0-4.0	12-22

* The yield (g) is the sum of 5 parallel experiments

substituents in the molecule (OH-group in NP and NH$_2$-group in NA) decreases the rate of nitro-compounds reduction. According to the data [26-30], the electron-donor amino groups in the molecule increase the electron density in nitro groups, and this effect manifests itself more strongly in the p-position, in comparison with the m-position.

Laboratory tests with increased reactants amounts are carried out to synthesize p-PDA, o- and p-AP under optimal process conditions on the most efficient and selective catalysts. In this case 50 g of a nitro compound are hydrogenated in 200 ml of the solvent (Table 4). The catalyst consumption is 0.02 % - 0.03 % of the active metal (Pd, Pd-Cu or Pd-Pt). The characteristics of the products obtained (T$_{boiling}$, T$_{melting}$, density) correspond to the reference values.

The results of Table 4 show that it is possible to obtain high amine yields of 90 % - 98.7 % in case of using relatively small amounts of the catalysts (0.48 g - 0.6 g of the catalyst in hydrogenation of 50 g of an aromatic nitro-compound). The process time using bimetallic catalysts is shorter than that in presence of a monometallic Pd-containing catalyst. The comparison referring to the hydrogenation of increased batches of compounds shows that n-NA reduction proceeds faster than that of p-NP

and much faster than that of o-NP. It should be noted that there are also ca 5 % - 7 % of o-aminocyclohexanol in the final products samples in case of the tests carried out with a catalyst supported on coal (Pd-Pt/C). For this reason, the yield of the target product, p-AP, is lower than expected (90 %).

The synthesized catalysts are studied by a complex of physicochemical methods. It is found that the surface area of the catalysts deposited on C is almost 2 times greater than that of the catalysts deposited on γ-Al$_2$O$_3$. The pores of the catalysts with γ-Al$_2$O$_3$ support are in the form of cylinders with a radius of 20 Å - 22 Å.

The XPS data showed that palladium on the coal is completely reduced to a zero-valence state, whereas on γ-Al$_2$O$_3$ palladium is not completely reduced. The binding energy of electrons Pd° 3d$_{5/2}$ Pd/C is 336.5 eV, which corresponds to Pd^{2+}.

Table 5 shows some characteristics of the catalysts samples. The carrier of Al$_2$O$_3$ and the catalysts deposited on it are investigated by scanning electron microscopy (Fig. 5). SEM data showed that the structure of the Al$_2$O$_3$ carrier is needle-like crystalline formations in the range 250-280 Å.

The data of hydrogen TPD (Fig. 6) in case of two-component metal catalysts deposited on a carrier shows
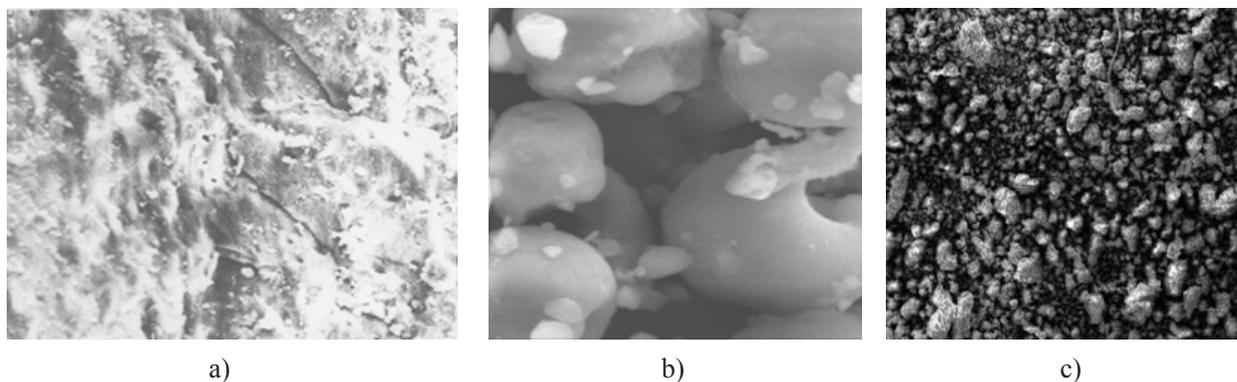
a)   b)   c)

Fig. 5. SEM-images of catalysts: a - γ-Al$_2$O$_3$, b - 2 % Pd/γ-Al$_2$O$_3$; c - 2 % Pd-Pt/γ-Al$_2$O$_3$.

Table 5. Characteristics of catalysts according to physicochemical data.

No	Catalyst	S, m²/g	d$_{particle}$, nm	a, nm
1	Pd/γ-Al$_2$O$_3$	165.0	5-18	γ-Al$_2$O$_3$ lines
2	Pd/C	350.0	12-25	
3	Pd–Pt/γ-Al$_2$O$_3$	209.0	5-18	γ-Al$_2$O$_3$ lines
4	Pd–Pt/C	380.0	12-25	
5	Pd–Pt/γ-Al$_2$O$_3$	162.0	5-18	γ-Al$_2$O$_3$ lines
6	Pd-Cu/C	400.0	12-25	
7	Pd-Cu/γ-Al$_2$O$_3$	160.0	5-18	γ-Al$_2$O$_3$ lines

Fig. 6. Thermodesorption of hydrogen from various catalysts with a linear increase in temperature within 0 - 750ºC: 1 - Rh/A1$_2$O$_3$; 2 - Pd/A1$_2$O$_3$; 3 - Rh-Pd(1:1)/A1$_2$O$_3$; 4 - Rh-Pt (1:1)/A1$_2$O$_3$; 5 - Rh-Pd(9:1)/A1$_2$O$_3$; 6 - Rh-Pt(9:1)/A1$_2$O$_3$; 7 - Pd-Ru(1:1)/A1$_2$O$_3$

that the number of forms of sorbed hydrogen characteristic for each of the components of the active phase does not change, but their ratio varies with the composition of the catalyst. It was found that hydrogen from Pd-Pt/ catalysts deposited on γ-Al$_2$O$_3$ is desorbed in the form of dissolved and strongly adsorbed.

CONCLUSIONS

The reduction of aromatic nitro-compounds (nitrobenzene, p-nitrodiethyl aniline, p- and m-nitroanilines, p- and o-nitrophenols) in a liquid phase using Pd and Pd-Pt catalysts deposited on various carriers is investigated. The shape of the kinetic curves of m-nitroaniline and p-nitrophenol demonstrate a strong poisoning of a part of the catalyst surface by the reaction product. The ratio of the adsorption coefficients shows that the hydrogenation products (the amines) have a stronger susceptibility to adsorb on the surface of the catalyst than that 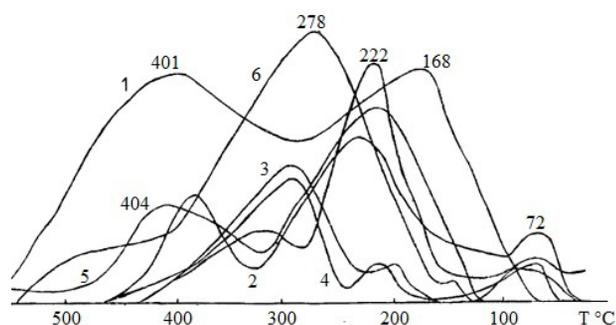of the initial compounds. The rate of the nitro-compounds hydrogenation decreases following the line: nitrobenzene> p-nitroaniline> m-nitroaniline> p-nitrodiethyl-aniline (p-nitrophenol) >> o-nitrophenol.

The synthesized catalysts provide obtaining amines as target products up to 89 % - 99 % under mild conditions.

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