Eng. Sci., 2023, **26**, 1001

Engineered Science
DOI: https://dx.doi.org/10.30919/es1001

Humic Acid Modified Applied Palladium Catalysts For Nitro Compounds Reduction

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Abstract

This work studies the possibility of using humic acids (HA) as a natural polymer-modifier for applied palladium catalysts. New catalysts based on palladium - HA fixed on the carrier bauxite-094 (B-094) have been synthesized and their catalytic properties in the process of reducing p-nitrodiethylaniline (PNDA) and potassium o-nitrophinolate (PtONPh) have been studied. Humic acid is a non-toxic, inexpensive, easily accessible high molecular weight polymer. Therefore, its use as a modifier polymer for applied palladium catalysts in the processes of hydrogenation of nitro compounds is very cost-effective and relevant as of today. This work presents the results of studies on different methods for the preparation of polymer metal catalysts. It has been shown that HA has stronger acid and sorption properties, greater branching and asymmetry of macromolecules. It has been established that the activity and stability of polymer-metallic complexes (PMC) based catalysts depend on the sequence of application of the active phase on the carrier. The largest specific surface area is characterized by the catalyst 1.0% Pd-HA (1.0%)/B-094, which exhibits the greatest activity and stability in the reduction reactions of PNDA and PtONPh. Considering that HA (polymer) and bauxite-094 (carrier) are materials of natural origin, the development of such catalysts is not accompanied by large economic costs, which is one of the main requirements for modern catalysts.

Keywords: Humic acids; Catalysts; Polymer-metallic complexes; Catalytic activity; Nitro compounds.
Received: 03 October 2023; Revised: 19 October 2023; Accepted: 20 October 2023.
Article type: Research article.

1. Introduction

Humic acid (HA) as a heterogeneous mixture of organic substances is found in peat, brown coal, streams, rivers, wetlands, lakes, and groundwater. The molecular structure of HA contains double bonds and aromatic rings bearing different functional groups such as carboxyl (-COOH), hydroxyl (-OH), amino (-NH2), quinonyl (-$C_6H_3O_2$). These functional groups can form water-soluble, colloidal and water-insoluble complexes with different properties of chemical and biological stability.[1-5]

With the development of chemistry, there is a need to create a new type of catalysts that combine the advantages of inorganic and organic ion exchangers. Such catalysts can be obtained by fixing on the surface of inorganic substances organic compounds containing ionic functional groups. As a carrier, natural mineral raw materials can be used, which are cheap, easily accessible and have adsorption and ion-exchange properties.[6,7] In this regard, it was of interest to prepare highly effective catalysts based on fixed HA complexes with group VIII metals with an inorganic matrix of natural origin. In the works,[8-16] high activity of palladium catalysts is noted. Polymers[15] containing trans –M-(CH_2–CH_2–$C_6H_4N)_2Cl$ fragments were obtained, where M is palladium and platinum. It was found out that nitro compounds are selectively and almost completely reduced to the corresponding amines, and palladium polymer complexes are more active than platinum complexes. The activity of the polymer complexes decreases with increasing molecular weight of the polymer. As the size of the macromolecules increases, the number of "loops" oriented perpendicular to the surface of the carrier and the thickness of the adsorption layer increases. It makes it difficult for reactants to access the active centers and takes more time

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to develop the catalyst. Modification of catalysts with higher molecular weight polymers leads to almost complete deactivation of catalysts, which is apparently related with the diffusion factor.

Thus, it follows from the above that the use of a polymer ligand in heterogeneous catalysts brings properties characteristic of linear macromolecules: swelling, sensitivity to the nature of the solvent, changes in the external environment. As a result, it is necessary to select the optimal conditions for the preparation of catalysts and carry out the process taking into account the activity of macromolecules.

In the works,[17,18] the hydrogenation of nitrobenzene, o-, m-, p-nitrotoluenes, nitro-, azo-, amino-, hydrazo- derivatives of p-, o-ethylnitrobenzene in the presence of palladium-containing polymer catalysts has been studied. It has been shown[11] that unlike the classical palladium catalyst on coal, palladium containing polytrimethylolmelamine has selectivity with respect to alkyl-nitrobenzenes, meanwhile the highest selectivity has been recorded during hydrogenation of o-ethylnitrobenzene.

Palladium-coated catalysts were obtained[18] by fixing palladium on a strongly acidic cation-exchange resin (KT1), weakly acidic cation exchanger (KT2), strong basic anion exchanger (KT3), weak basic anion exchanger (KT4) and chelate resin (KT5) and their activity in the hydrogenation of nitro compounds was studied. Activity decreases in the row as follows: KT3 > KT1 > KT4 ≈ KT2 >KT5.

In order to improve the performance (or activity, stability) of the catalysts, it was necessary to develop a preparation method in which the bulk of the active metal was located on the outer accessible surface of the carrier. The implementation of this method is possible by using the properties of palladium chloride (II) to form polymer complexes by changing the pH of the aqueous solution.

We studied the possibility of using humic substances (HS) as a natural polymer-modifier for applied palladium catalysts, as well as synthesized new catalysts based on palladium - potassium humate, fixed on the carrier bauxite-094 (B-094) and studied their catalytic properties in the process of reducing p-nitrodiethylaniline (PNDA) and potassium o-nitrophinolate (PtONPh).

2. Experimental part

2.1 Reagents

PNDA – $C_{10}H_{14}NO_2$, M = 194.23 g/mol, appearance – yellow crystals, soluble in alcohols, technical grade (TU 6-14-11-1-84), melting point 350-351K; o-nitrophenol $C_6H_5NO_3$, M =139.1g/mol, appearance – pale yellow needle crystals, melting point = 45.3°C; boiling point = 216°C; d_{20}=1.2942; n_D^{20}=1.5723; soluble in water, Ethanol (chemically pure), Na_2PdCl_4, HCl (chemically pure), HNO_3 (chemically pure), KOH (chemically pure). Bauxite-094 with the following chemical composition was used as an inorganic carrier: Al_2O_3-35.1%; SiO_2-15.1%; Fe_2O_3-23.7%. Bauxite consists of gibbsite, kaolinite, and various aluminosilicates, so it has a variety of physical, mechanical and chemical properties, which makes it possible to use it as a carrier for the synthesis of catalysts.

2.2 Preparation of applied palladium catalysts

100cm^3 of distilled water is poured into a beaker with a volume of 500cm^3, the carrier and Na_2CO_3 are poured until a pH of 9-10 is received and stirred at room temperature on a magnetic stirrer. The suspension is stirred for 10-15 minutes until the carrier is completely wetted. The calculated amount of Na_2PdCl_4 is adjusted with distilled water to 50 ml, and then this solution is transferred by the impregnation method to a beaker with a stirred suspension of the carrier. In order to achieve complete precipitation of palladium, the suspension is stirred for one hour. The completeness of palladium precipitation is checked by a negative reaction with potassium rhodanide. The catalyst is washed with distilled water until neutral reaction, filtered, dried in a vacuum oven at a temperature of 363K for three hours.

2.3 Preparation of Pd-catalysts modified with HA applied on B-094.

Applied on bauxite-094 modified with HA palladium catalysts were prepared as follows: a sample of bauxite (3 g) was added to 150 ml of distilled water, then a solution of HA (0.7-2.0 wt.% relative to the weight of the carrier) was added with stirring, and at the same time an aqueous solution of Na_2PdCl_4 (1.0 wt.%) was added. The resulting catalysts were stirred for 2 hours and then washed, filtered and dried at 383K for two hours.

2.4 Hydrogenation of PNDA and PtONPh

Hydrogenation was carried out in a thermostatically controlled catalytic "chamber" at atmospheric pressure and a temperature of 20°C. Simultaneously, the reaction rates (amount of absorbed hydrogen per unit time, cm^3/min) and the catalyst potential (mV) relative to the calomel reference electrode were recorded. Before the reaction, the catalyst was treated with hydrogen in a solvent ($V = 25$cm^3) until a reversible hydrogen potential was reached. Hydrogenation was carried out in the kinetic mode (700-800 pumps/min).

2.5 Analysis of catalysts

The specific surface area was determined by the BET equation in the relative pressure range P/P_0 =0.05-0.35 (the cross-sectional area of the argon molecule was taken equal to 13.8 Å) In the range of values P/P_0 =0.05-0.35 for all the studied catalyst samples, the BET graphs turned out to be linear, which made it possible to calculate the volume of the mono-layer and the values of the specific surface area of the catalysts.[19]

2.6 Analysis of raw materials and products

Determination of total moisture was carried out according to GOST 11014-2001 "Brown coals, hard coals, anthracite and oil shales. Accelerated methods of moisture determination". A sample weight of 2 g, selected from shales with a particle size of 2 mm-125 µm, was dried in a BINDER drying cabinet at a temperature of (105±5)ºC, the mass fraction of moisture was calculated by weight loss.

Ash content of combustible fossils was determined according to GOST 11022-95 "Solid mineral fuel. Ash determination". A 2 g shale sample was burned in a SNOL-8.2/1100 muffle furnace at a temperature of (815±10)ºC and held at a predetermined temperature to constant weight. Ash content was calculated from the weight of the residue after calcination.

The yield of volatile substances was determined by heating a 1g sample in a porcelain crucible with a ground lid in a SNOL-8.2/1100 muffle furnace at a temperature of 850ºC for 7 minutes.

The yield of humic substances from coals was determined according to GOST 9517-94 (ISO 5073-85) "Solid fuel. Methods for determining the yield of humic acids".

2.7 Determination of HA functional groups

Determination of HA functional groups. The determination of carboxyl, carbonyl, phenolic groups, as well as the dissociation constants of acid groups was carried out according to the procedure specified in the reference.[20]

Determination of the elemental composition, namely, the content of carbon, hydrogen, nitrogen, sulfur and oxygen was carried out on the EMA 502 elemental microanalyzer. Analysis of CHNS-O using the EMA 502 elemental microanalyzer helps to determine the structure of an unknown compound, as well as to assess the structure and purity of the synthesized compound. The results are automatically calculated using EMASoftTM software that receives real-time data from the EMA 502 elemental analyzer.

3. Results and discussion

In this work, HA was used as a natural polymer-modifier for applied palladium catalysts. Catalysts based on the palladium-potassium humate complex fixed on carrier B-094 were synthesized and their catalytic properties were studied. The physical and chemical characteristics of coal are given in Table 1, from which it can be seen that the moisture content in Oy-Karagay coal is 7.8%, ash content is 12.0%, as well as the mineral component (wt.%): SiO_2 30.2, Al_2O_3 25.8, Fe_2O_3 13.5, CaO 19.6, MgO 2.9, Na_2O+K_2O 1.0, SO_3 2.0. According to the elemental composition, the ratio C:H = 15.8; O/C = 0.20-0.26, the content of volatile substances V^{daf} = 35.8%, coal is suitable for the production of humic acids.[21,22]

Based on both our experimental data[19,21,22] and the results obtained by other research teams the following parameters were selected as the technological parameters of the HA extraction process from the coal of the Oy-Karagay deposit: the concentration of the NaOH solution is 1.0%, the temperature of heating the reaction mixture is 80°C, the processing time is 120 minutes, the ratio of coal and alkali solution is 1:50 The yield of humic substances was 43%. HA contains 7.2% moisture and 2.3% ash content. The specific area of HA is 18.43 m^2/g, the volume of the mono-layer is 4.23 m^2/g (Table 1).

Table 1. Characteristics of coal and humic acids.

Characteristics	Value, % wt
Coal of Oy-Karagay deposit	
Moisture content, W, %	7.8
Ash content, A, %	12.0
Volatile substances yield, V, %	35.8
Elemental composition, wt.%:	
C	78.49
H	4.97
N	0.10
S+O	16.44
Low heating *value,* Q_i, MJ/kg	15.6
High heating *value,* Q_s, MJ/kg	28.5
Output of humic substances*, %	43
Humic acid	
Moisture content, W^a, %	7.2
Ash content, A^a, %	2.3
Specific surface area, m^2/g	18.43
Monolayer volume, m^2/g	4.23

The elemental analysis data presented in Tables 1 and 2 shows that the elemental composition of coal and HA is different, i.e. there is a decrease in carbon (from 78.49 to 58.63%), hydrogen (from 4.97 to 4.20%), as well as an increase in nitrogen (from 0.10 to 1.47%), sulfur and oxygen (from 16.44 to 35.70%), respectively. The results of the elemental analysis allow to characterize some features of the HA obtained from coal and provide information on the

Table 2. Elemental composition of HA.

Sample	Content of elements, % wt				Content of elements, % at				Atomic ratios		
	C	H	O+S	N	C	H	O	N	H/C	O/C	N/C
HA	58.63	4.20	35.7	1.47	50.84	35.57	12.5	1.09	0.7	0.25	0.02

principles of their structure. For these purposes, it is more convenient to use not the percentage expression of the composition of humic acids established in the analysis, but the atomic ratios of the elements, composing the simplest formulas and applying the principles of graphical and statistical analysis

The atomic ratios H/C, O/C, N/C reflect the number of hydrogen, oxygen and nitrogen atoms per carbon atom in the molecule (particle) of humic substances. The smaller they are, the greater the role of carbon atoms in the construction of the molecular structure. An important indicator is the H/C ratio, which characterizes the degree of aromaticity or unsaturation (at low values) or aliphaticity (at high values). In our case, HA has values of this ratio of 0.7, which indicates the predominance of aromatic fragments in their composition. One of the characteristics of humic substances is the degree of oxidation – a value showing the ratio of oxidative and reducing fragments in the molecule. Humic acids are characterized by a value of the degree of oxidation, close to zero (0.25), which indicates a high redox buffering and chemical stability of these substances.

The quantity of carboxylic, phenolic and carbonyl groups of the studied substances were determined. The results of the functional analysis are shown in Table 3.

Table 3. Acid properties of coal and humic acids.

Sample	pK_α	Functional composition, mg-eq/g			
		[COOH+OH]	[COOH]	[OH]	C=O
Coal	9.52	6.4	2.9	3.5	1.45
HA	6.88	7.0	2.7	4.3	1.9

The macromolecule of coal and HA contain many functional groups that differ in their degree of acidity. Table 3 shows that the total content of acidic groups in coal is 6.4 mg-eq/g, including carboxyl groups – 2.9 mg-eq/g, phenolic hydroxyls – 3.5 mg-eq/g and carbonyl groups – 1.45 mg-eq/g. The total acidity is 9.52 mg-eq/g. And the total acidity of HA is 6.88 mg-eq/g due to the content of phenolic (4.3) and carbonyl groups (1.9). The total content of acidic groups of HA is 7.0 mg-eq/g.

When preparing the catalysts, the sequence of application of the active components, *i.e.* Pd and HA on the carrier (B-094), was varied. The process was carried out by impregnation by five different methods:

Method 1 Simultaneous application of HA and Pd on the carrier. The carrier (3 g) was filled with 150 ml of water, then, with stirring, solutions of HA (1.0 wt. %) and Na_2PdCl_4 (0.8 wt.%) were added. %). The mixture was stirred for 2 hours, then washed, filtered and dried at 383K for 2 hours.

Method 2 Alternate application of HA and Pd on the carrier. Bauxite-094 was stirred with HA solution for 2 hours, then Na_2PdCI_4 solution was added by sprinkling. The mixture was stirred for 2 hours, after which the catalyst was washed, filtered and dried.

Method 3 Bauxite-094 was stirred with Na_2PdCl_4 solution for 2 hours, then sprinkled with HA solution. The mixture was stirred for 2 hours, after which the catalyst was washed, filtered and dried.

Method 4 The catalyst was prepared similarly to the previous one, but after mixing the carrier with both components, the mixture was left in the mother liquor for 10 hours.

Methods 5 Application of pre-mixed HA and Pd solutions on the carrier. At the calculated concentration, the HA and Na_2PdCI_4 solutions were pre-mixed with each other, then this mixture was added to the carrier by sprinkling under stirring. The mixture was stirred for 2 hours, after which the catalyst was washed, filtered and dried at 383K.

Catalysts prepared by such methods were tested for activity in PNDA and PtONPh reduction reactions. The results of the studies are shown in Fig. 1.

From Fig. 1, it can be seen that the most active is the catalyst, which is prepared according to method 1, and the least active is the catalyst prepared according to method 5. As a result of the reduction reaction of PNDA and PtONPh, the activity of the jointly precipitated catalyst (method 1) is 2-3 times higher compared to other methods of catalyst preparation. And we also see that the catalysts prepared by methods 4-5 reduce PNDA and PtONPh at a rate lower (17.9; 12.3 and 14.0; 8.7) than the catalyst without HA (21.2 and 15.2, respectively).

As a result of the research, it was established that the activity of the PMC-based catalyst (polymer-metal complexes) developed by us depends on the method of its preparation. When Pd and HA are applied on the carrier together, the stereoregular orientation of the active phase particles acquires an optimal structure and, thereby, the activity of the catalyst prepared by said method is explained.

The catalytic properties of the modified catalysts depending on the amount of application of the active phase

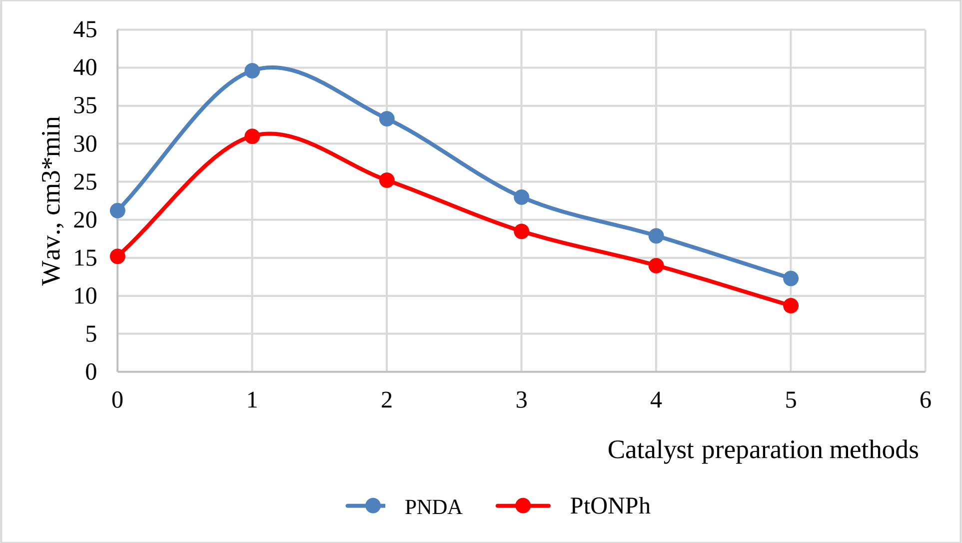

Fig. 1 Dependence of catalyst activity on the preparation method in PNDA and PtONPh reduction reactions (P_{atm}, T = 333K, m_{Cat} =0.1g, m_{PNDA} = 0.29g, m_{PtONPh} =0.21g, V_{H2} = 100 cm^3).

palladium.

To select the optimal content of palladium in the catalyst, the dependence of the specific reduction rate of PNDA and PtONPh on the concentration of the active phase was studied. The content of HA in the catalyst is 1.0 wt% relative to the weight of the carrier. The palladium concentration values in the catalysts were as follows: 0.5; 0.8; 1.0; 1.5; and 3.0 wt% (relative to carrier's weight). The synthesized catalysts were tested in the reduction of PNDA in ethanol and PtONPh in 0.1N KOH. Results are presented in Table 4.

Table 4 shows that in the reduction reactions of PNDA and PtONPh, with an increase in the concentration of palladium in the catalyst from 0.5 to 1.0 wt.%, the specific rate increases to 86.4 and 60.8 dm^3/min*g Pd, respectively, with a further increase in the concentration of palladium in the catalyst to 3.0 wt.%, the value of the specific reaction rate drops to 55.0-49.6 dm^3/min*g Pd, while Δφ changes slightly. Based on the results obtained, it can be concluded that the optimal concentration of palladium in the catalyst is 1.0 wt.%.

We determined the surfaces of the obtained catalysts using the BET method.[19] Table 4 shows the specific surface area (S_W) values of the catalysts. As can be seen from Table 1, for the polymer – HA extracted from the coal of the Oy-Karagay deposit, the specific surface area was 18.43 m^2/g. On catalysts, when varying palladium concentrations from 0.5 to 1.0%, the specific surface area of the catalyst increases to 45.31 m^2/g (Table 4). Perhaps, the particles of the active phase are not completely fixed on the surface of the polymer and the carrier, but agglomerate on each other, as a result, the specific area of the catalyst decreases.

3.1 Catalytic properties of modified catalysts depending on the amount of application of the active phase humic acid (HA)

This section investigates the effects of the concentration of a natural polymer – HA, since humic acid acts as a natural polymer in the formation of polymer-metal complexes. The HA content in the catalyst ranged from 0.5 to 2.0 wt.%. The concentration of the active phase was 1.0 wt.%. The catalysts prepared by the first method were tested in PNDA and PtONPh reduction reactions. Obtained results are presented in Table 5.

Table 4. Specific activities and surfaces of catalysts from the concentration of the active phase during the reduction of PNDA in alcohol and PtONPh in 0.1N KOH (T = 333K, P_{atm}, m_{Cat} =0.1g, m_{PNDA} = 0.29g, m_{PtONPh} =0.21g, C_{HA} =1.0%).

		PNDA		PtONPh		
Catalyst	Pd, wt%	Wspecific, dm^3*H_2/min*g Pd	Δφ, mV	Wspecific, dm^3*H_2/min*g Pd	Δφ, mV	S, m^2/g
Pd/B-094	0.8	21.2	139	15.2	290	24.0
Pd-HA /B-094	0.5	32.4	142	43.8	286	32.64
	0.8	47.0	148	46.8	280	44.46
	1.0	86.4	160	60.8	300	45.31
	1.5	63.7	153	51.0	278	44.17
	3.0	55.0	157	49.6	282	44.09

Table 5. The activity of catalysts depending on the concentration of the natural polymer during the reduction of PNDA in alcohol and PtONPh in 0.1N KOH (T=333K, P_{atm}, $m_{Cat.}$ = 0.1g, m_{PNDA}=0.29g, m_{PtONPh}=0.21g).

Catalyst	HA, %	PNDA		PtONPh		S m^2/g
		Wspecific, dm^3/min	Δφ, mV	Wspecific, dm^3/min	Δφ, mV	
0.8% Pd/B-094	-	21.2	139	15.2	290	24.0
1.0% Pd-HA/B-094	0.5	39.0	140	32.6	280	40.25
	0.75	64.0	160	43.2	320	36.85
	1.0	86.4	160	60.8	300	45.31
	1.5	63.6	148	59.2	320	40.30
	2.0	31.8	150	35.2	280	43.53

Table 6. Stability of catalysts in PNDA reduction reactions in ethanol at T=333 K.

Catalysts	W, cm^3 H_2/min							
	1	2	3	4	5	6	7	8
0.8% Pd/B-094	21.4	18.4	14.5	12.5	11.2	10.0	8.3	7.3
1.0% Pd- HA (1.0%)/B-094	86.6	84.3	77.6	74.3	68,3	66.5	63.2	47.3

From the data in the table, it can be seen that the maximum reduction rate of PNDA is observed when the content of potassium humate in the catalyst is 1.0 wt.%. In the presence of this catalyst, the reaction rate is 4 times greater than in the presence of Pd/B-094 catalyst unmodified with potassium humate. When varying the concentration of the polymer - HA from 0.5 to 1.0%, it can be seen that the specific surface area of the catalyst increases from 40.25 m^2/g to 45.31 m^2/g. With an increase in the concentration of the polymer to 2%, the specific area changes slightly (Table 5). It follows that the size of the catalyst surface depends not only on the composition/nature and concentration of the polymer-modifier that is part of the catalyst, but also on the concentration of the active phase, which explains the catalyst activity of 1.0% Pd-HA (1.0%)/B-094. Thus, when modifying the 1% HA catalyst, the catalyst activity increases, therefore, the optimal concentration of HA is 1.0 wt.%.

3.2 Catalyst stability

One of the most important characteristics of catalysts is their stability. Most of the catalysts used in industry have an insignificant service life; therefore, the stability of 0.8% Pd /B-094, 1.0% Pd- HA (1.0%)/B-094 catalysts were studied when reducing consecutive 8 PNDA weights. The findings of the macro-structure analysis are summed up in Table 6.

The table shows that the catalyst activity of 0.8% Pd- /B-094 after 8 experiments decreases by 66%, and the activity of applied palladium catalysts modified with HA decreases by 45%. The first sample of the PNDA is reduced at a rate of 86.6, the second sample at a rate of 84.3, and the third sample at a rate of 77.6 cm^3 H_2/min. The eighth PNDA sample is reduced at a rate of 47.3 cm^3 H_2/min. The total yield of amine is 96.0%. From the experimental data on the stability of catalysts, it follows that the activity and stability of 1.0% Pd-HA/B-094 catalyst is higher due to the modifier polymer – HA, since the catalyst without the addition of HA was less stable by more than 20%. Considering that HA (polymer) and bauxite-094 (carrier) are materials of natural origin, the development of such catalysts is not accompanied by large economic costs, which is one of the main requirements for modern catalysts.

4. Conclusions

On the basis of the research work carried out, the following conclusions were made:

- Optimal conditions for the extraction of humic acids from the coal of the Oy-Karagay deposit have been established. The technical characteristics, elemental and functional compositions, acidic properties of coal and HA have been determined. It has been found that HA has stronger acid and sorption properties, greater branching and asymmetry of macromolecules.
- For the first time, a method for the synthesis of highly active, stable palladium catalysts based on polymer-metallic complexes (PMC), palladium and HA extracted from Oy-Karagay coal has been developed.
- It has been established that the activity and stability of PMC-based catalysts depend on the sequence of application of the active phase on the carrier. The greatest activity in the reduction reactions of PNDA and PtONPh is shown by the catalyst, where palladium and polymer were applied together to bauxite-094. The optimal concentrations of the active phase and polymer in the catalyst has been determined as follows: palladium – 1.0 wt.%, HA – 1.0 wt.%.
- The largest specific surface area is characterized by a catalyst 1.0% Pd-HA(1.0%)/B-094 (45.31 m^2/g), which exhibits the greatest activity and stability in nitro compounds reduction

reactions.

Acknowledgment

This research has is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP09057905 «Development of technology for the production and use of specific organic substances from coal and oil shale deposits of RK, as a source of naturally occurring catalysts and antioxidants»).

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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