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NICKEL NANOCATALYST FOR HYDRODECHLORINATION OF POLYCHLORINATED BIPHENYLS

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Currently, nanomaterials are an important class of materials in the field of synthesis of efficient and selective catalysts with desired properties due to their unique physical and chemical properties. The presence of nanosized particles of transition metals undoubtedly improves the course of the hydrodechlorination of polychlorinated biphenyls (PCBs) and makes it possible to reduce the content of the noble metal in the catalyst. In order to obtain active and stable heterogeneous catalysts for the neutralization of persistent organic pollutants (POPs), the correct choice of carrier and method of catalyst synthesis is required. In this work, the synthesis of a nickel nanocatalyst was carried out using the wet impregnation method for the hydrodechlorination of PCBs. Commercial activated carbon grade BAU-A was pre-modified with hydrochloric acid and used as a carrier (AC_m) of the catalyst. Using modern physical and chemical methods, the main properties of the synthesized nanocatalyst were investigated. The IR spectroscopy has established that the carboxyl and carbonyl groups of AC_m are the main functional groups that fix nickel in the bulk of the carrier. The nickel nanocatalyst has a developed surface, where nickel nanoparticles are deposited in micro- and mesopores of the carrier. The degree of conversion of 2,2',3,3',4-pentachlorobiphenyl is 84.21%, which indicates the catalytic activity of nickel nanocatalysts with respect to POPs.

Keywords: *nanocatalyst, persistent organic pollutants, polychlorinated biphenyl, nickel nanoparticles, activated carbon.*

1. INTRODUCTION

The halogen-containing organic compounds are widely used in many industries as target and intermediate products. Due to its high toxicity and chemical stability, a lot of halogenated organic compounds are recognized as persistent organic pollutants (POPs) and banned from usage by the World Health Organization. Also, on May 22, 2001, the Convention on persistent organic pollutants was signed in Stockholm, which aims to reduce and completely eliminate the production, usage, emissions and storage of existing stocks of POPs [1]. Kazakhstan ratified this convention by the law of the Republic of Kazakhstan dated June 7, 2007.

The stocks of surplus halogenated by-products and POPs that have been accumulated up to these days need to be disposed of in an environmentally sound manner, which necessitates the development of methods for utilizing halogenated organic substances and converting them into less hazardous compounds.

Kazakhstan ranks second after Russia in terms of the amount of POPs waste. Due to the heterogeneity of the composition of polychlorinated biphenyls (PCBs) related to POPs and the variety of methods for its disposal, it is extremely important to select, improve existing ones and develop new effective and environmentally friendly methods for the disposal of POPs in order to turn it into useful products. A large number of POPs neutralization methods have been studied [2–6], the choice of which depends on the state of aggregation of the material to be disposed of, the concentration of POPs, technological and environmental features of the ongoing processes. The possibility of formation of dioxin-like by-products during the disposal of POPs necessitates the implementation of strict control of the technological process.

There is an increased share of studies on the processes of reductive dechlorination of PCBs due to the possibility of use new types of catalysts obtained using nanomaterials and nanotechnologies and the tightening of requirements for analytical control over the formation of by-products of polychlorinated dibenzofurans (PCDF) and dibenzodioxins (PCDD). The development of a reductive method for dechlorination of PCBs is facilitated by the search for active, selective and efficient catalysts. The monitoring of literature sources has shown that palladium-containing catalysts obtained using nanomaterials and nanotechnologies on inert carriers show the highest activity and selectivity in the reductive transformations of chlorine-containing compounds [7–11]. Selectivity depends on the type of catalyst, carrier and operating temperature. Palladium content in catalysts, in many cases ≥10% (by mass) [12]. The high cost of palladium contributed to the search for methods to reduce the cost of catalysts at the expense of metals with low cost characteristics.

A comparative study of the catalytic properties of palladium, platinum, and nickel deposited on a “Sibunit” carbon carrier was inserted in reductive hydrodechlorination of PCB, DDT, and triclosan under mild conditions at room temperature and a hydrogen pressure of 1 atm [13]. Hydrodechlorination of POPs with hydrogen using various catalysts, including based on copper and nickel nanoparticles inserted on activated carbon showed good catalytic activity [14–16]. Therefore, nickel-based catalysts are no less attractive objects for PCB nanocatalysis. In addition, it should be noted that nickel-based catalysts for PCB hydrodechlorination are poorly studied.

This work is devoted to the synthesis of a nickel catalyst inserted on activated carbon modified with hydrochloric acid, also to the study of the physical, chemical properties and catalytic activity with respect to PCBs.

2. EXPERIMENTAL SECTION

2.1 Materials and methods

2.1.1 Materials

The following reagents were used in the work: nickel nitrate, $Ni(NO_3)_2•6H_2O$ (99,9%, Sigma Aldrich), sodium tetrahydroborate, $NaBH_4$ (99,9%, Sigma Aldrich), sodium hydroxide NaOH (Sigma-Aldrich), Arochlor 1254 (2,2',3,3',4 – pentachlorobiphenyl) (certified solution of arochlor in hexane, concentration 100 µg/ml, to work in accordance to MG 4.1.1023-01). These reagents were used without further purification. The commercial charcoal of the BAU-A brand, modified according to the method [17], was used as a carrier. Hydrochloric acid, HCl (ST 11125-84, LLC MK "Magna", Russia) was used in order to modify activated carbon.

2.1.2 Preparation of catalysts

The impregnation method was used to obtain a Ni/activated $\text{carbon}_{\text{modified}}$ (AC_m) (hereinafter, Ni/AC_m) catalyst based on BAU-A grade carbon material modified according to the procedure [12–13]. In the obtained catalysts, the content of the active phase of nickel was 10 wt. % by weight of the catalyst ($10Ni/AC_m$). The preparation of the catalyst was relied on the procedure [18].

2.2 FTIR spectroscopy

The chemical structure of the catalyst was studied by IR spectroscopy. FTIR analysis was performed on a spectrometer FTIR FT-801 (Simex, Russia), with a resolution of 1 cm^{-1} and a wavelength 500–4000 cm^{-1} according to the standard procedure with the production of a tablet with potassium bromide in a ratio of 1/10 substances, at a temperature of 25 °C and a number of scans of 100. Before use, potassium bromide was crushed and calcined at 200 °C for 3 hours.

2.3 Scanning electron microscopy

The morphology and structure of the $10Ni/AC_m$ catalyst were studied using a high-vacuum scanning electron microscope (Zeiss Auriga Crossbeam 540, Germany). The elemental composition of the carrier and catalysts was determined on an energy-dispersive particle distribution analyzer (Thermo Fisher Scientific, USA).

2.4 Transmission electron microscope

The sizes of nickel nanoparticles were obtained using transmission electron microscopy (TEM) (JEM 1400 JEOL, Japan) with a resolution of 0.38 nm, an accelerating voltage of 120 kV, with a high-resolution digital camera (CCD Morada, OLYMPUS). Before TEM studies, the samples were crushed in an agate mortar, then the suspension of the alcohol solution of the samples was subjected to ultrasonic dispersion at a frequency of 44 kHz on an USDN-2T instrument (Electron, Russia), followed by fixing on a perforated carbon film deposited on a copper grid. Further, after drying measurements were taken. By statistical calculation of the particle sizes in the TEM image, the distribution and average particle size of the synthesized catalysts were determined.

2.5 TGA analysis

The thermal characteristic of the $10Ni/AC_m$ catalyst was studied on a differential thermogravimetric analyzer STA449C (NETZSCH, Germany) in an argon atmosphere within the temperature range of 30±5–700±5 °C. The heating rate was 10±1 °C/min. The mass of the samples was about 20±2 mg.

2.6 Adsorption porosimetry

The textural characteristic of the synthesized catalyst was determined using adsorption porosimetry (low-temperature nitrogen adsorption) on Autosorb 1 (Quantachrome Instruments, USA) and ASAP-2020 (Micromeritics, USA) devices, after preliminary vacuum for 3 hours, at a temperature of 220–250 °C for degassing samples, followed by mathematical processing of experimental data by BET and BJH.

2.7 Catalytic activity

The catalytic activity of the catalyst was studied in a flow reactor (Buchiglasuster, Switzerland) according to the procedure [15, 19].

2.8 Chromato-mass spectrometer

In order to identify the catalyst products an Agilent (GC 7890A, MS 5975C) chromato-mass spectrometer with a quadrupole mass spectrometric detector (GC-MSD) at an electron energy of 70 eV was used, using an HP-5MS quartz capillary column (30 µm × 0.25 µm × 0.25 µm); carrier was helium gas, division ratio 1:50, flow rate 1.0 cm^3/min. Temperature: initial 40 °C (holding 3 min), 290 °C at 10 °C/min (holding 20 min) and inlet temperature 250 °C.

3. RESULTS AND DISCUSSION

3.1 Physical and chemical properties of the 10Ni/ACm catalyst

Comparative IR spectra of the BAU-A carrier modified with hydrochloric acid and the $10Ni/AC_m$ catalyst are shown in Figure 1. Shifts in the absorption bands of functional groups in the IR spectra indicate the interaction of the catalyst components. Thus, the appearance of an intense absorption band of the stretching vibration, 872 cm^{-1} in the spectrum of the $10Ni/AC_m$ catalyst, associated with O–Ni– and the shift of the absorption band from 1713 cm^{-1} to 1558 cm^{-1}, indicates the fixation of nickel into the carrier through the carboxyl group AC_m (Figure 1). Also, the shift of the absorption bands from 1166 cm^{-1} to 995 cm^{-1} indicates the formation of the Ni/AC_m catalyst through the C=O carbonyl functional group. Thus, according to the result of IR spectroscopy, it can be assumed that nickel ions interact with the carboxyl and carbonyl groups of the AC_m carrier.

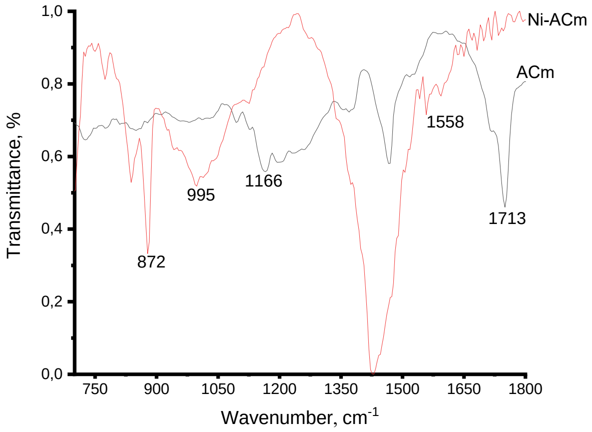
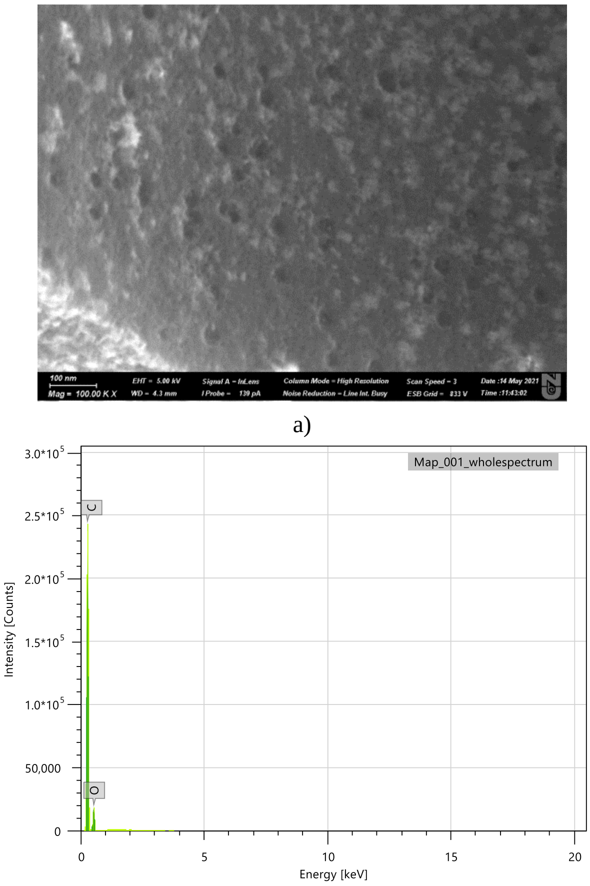


Figure 1. IR spectra of the 10Ni/ACm catalyst and activated carbon modified with hydrochloric acid ACm



a)

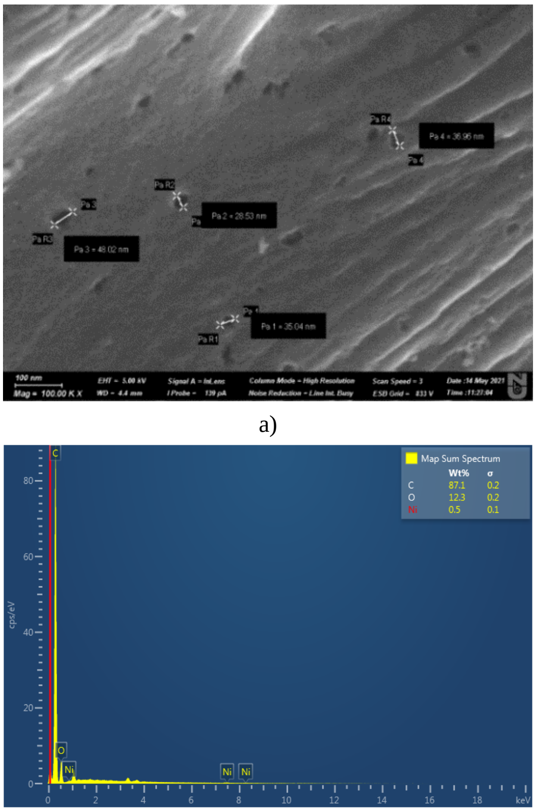
b)

Figure 2. SEM image of: (a) modified activated carbon grade BAU-A – ACm; (b) Energy dispersive analysis of the distribution of carrier particles

The presence of nickel in the catalyst was confirmed by using SEM with an energy-dispersive particle distribution analyzer, as well as TEM research methods. SEM images of the original AC_m carrier and the 10Ni/AC_m catalyst obtained on its basis are shown in Figures 2 and 3. The morphology of the 10Ni/AC_m catalyst is close to the morphology of the carrier BAU-A activated carbon modified with hydrochloric acid (Figure 2a). The carrier contains 83.89% carbon and 16.11% oxygen (Figure 2b and Table 1). Energy dispersive analysis indicates the presence of carbon 87.1%, oxygen 12.3% and nickel 0.5% (Figure 3b). The size of nickel nanoparticles varies within 28.53–48.02 nm. The decrease in the oxygen content is possibly associated with the interaction of nickel with the carboxyl and carbonyl functional groups of the carrier, which was confirmed by IR spectroscopy.

Table 1. Elemental composition of modified activated carbon grade BAU-A

№	Element	Line	Mass%	Atom%
1	C	K	83.89±0.09	87.40±0.09
2	O	K	16.11±0.14	12.60±0.11
TOTAL			**100.00**	**100.00**



a)

b)

Figure 3. SEM image of: (a) 10Ni/ACm catalyst; (b) energy dispersive analysis of the distribution of catalyst particles

The formation of nickel nanoparticles on a carbon carrier was confirmed by transmission electron microscopy (Figure 4). Most of the nickel particles in the obtained 10Ni/AC_m catalyst are spherical and small in size (30.33–34.77 nm). Spherical clusters of nickel nanoparticles in the form of agglomerates are distributed in the carrier volume (Figure 4). From the micrograph of the nanoparticles, one can see the presence of light channels that appear during the migration of nickel particles. This is confirmed by previous studies [20].

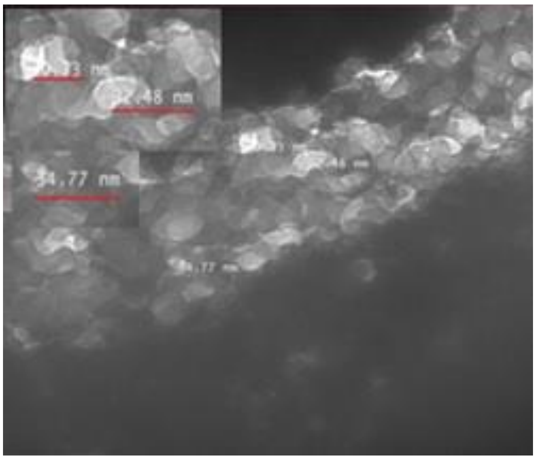


Figure 4. TEM image of the 10Ni/AC$_m$ nanocatalyst

Figure 5 shows the results of thermogravimetric analysis of the AC$_m$ carrier and 10Ni/AC$_m$ catalyst.

The main decrease in the weight of the catalyst occurs in the temperature range of 30-150°C and 400-700°C. The weight reduction in the low temperature zone, i.e. between 30–150 °C, due to the release of surface and adsorption water (Figure 5). Also, weight reduction within the temperature range of 400–700 °C is associated with the destruction of hydrocarbon compounds. The establishment of an equilibrium state is between 150–400 °C relative to the slow decrease in the mass of the carrier AC$_m$, shows some thermal stability of the functional groups, with fixed nickel nanoparticles (Figure 5).

The specific surface area of the 10Ni/ACm catalyst increases two times to that of the AC$_m$ support and is 541.518 m^2/g (Table 2). The pore size increases by almost 20 times, which is in good agreement with the data obtained from TEM analysis, which established additional channels as a result of the migration of nickel nanoparticles. The total pore volume of the catalyst is reduced by 1.4 times. This is due to the fixation of nickel nanoparticles in the pores of the carrier (Table 2).

Table 2. Textural characteristics of the 10Ni/AC$_m$ catalyst

Sample	**Specific pore surface SW, m^2/g**	**Pore size Dv(r)$_{\text{Pore Radius}}$, nm**	**Total pore volume V$_{\text{micro}}$, ml/g**
AC$_m$	233.8	0.19	122.12
Ni/AC$_m$	541.518	19.172	87.984

The N$_2$ adsorption isotherm for the 10Ni-AC$_m$ catalyst is characterized by type IV, typical for porous materials (Figure 6) [21]. The P/P$_o$ hysteresis loop is associated with capillary condensation in mesopores, which establishes the presence of both micro- and mesopores.

The pore distribution of the 10Ni/AC$_m$ catalyst and the AC$_m$ carrier has a similar character (Figure 7). Modified carrier and catalyst contain mesopores up to 19 nm and macropores 26 nm in size.

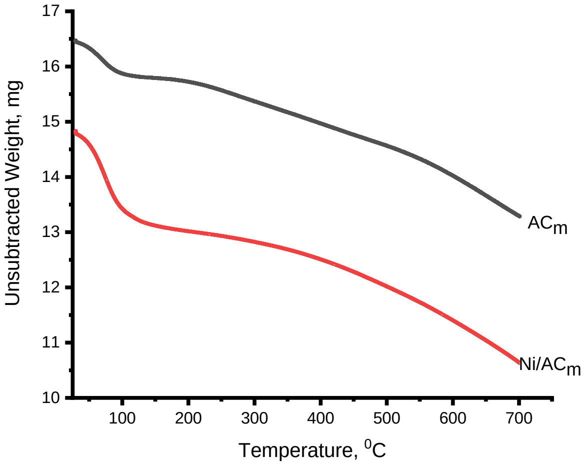


Figure 5. TGA of the 10Ni/AC$_m$ catalyst and activated carbon modified with hydrochloric acid AC$_m$

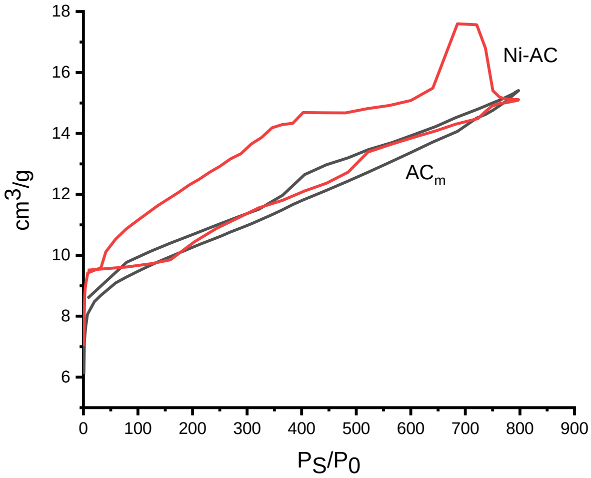


Figure 6. Adsorption-desorption isotherm of N$_2$ catalyst 10Ni/AC$_m$ and activated carbon modified with hydrochloric acid AC$_m$

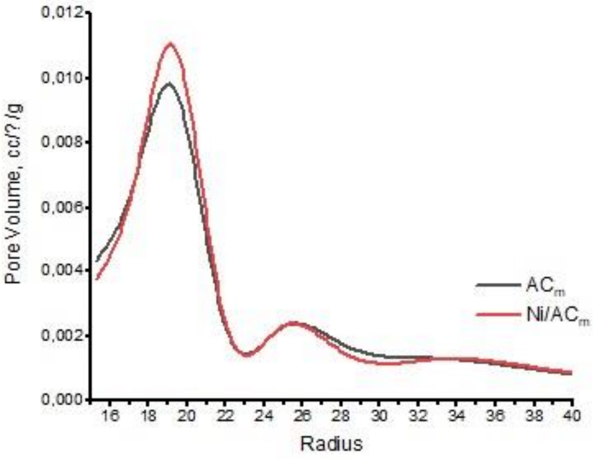


Figure 7. Pore size distribution for 10Ni/AC$_m$ catalyst and AC$_m$ activated carbon modified with hydrochloric acid

3.2. Catalytic activity

The obtained catalyst was tested in the reaction of PCB hydrodechlorination in a flow system with a fixed catalyst bed using methanol and hydrogen at a temperature of 25 °C and stirring for 5 hours. At the end of the hydrodechlorination reaction, magnesium sulfate was added to separate the organic part, then the catalysis product was obtained by centrifugation. The aliquot taken from the filtrate was diluted with hexane and analyzed to determine the reaction product. The chromatogram obtained as a result of identification is shown in Figure 8. The 10Ni/AC$_m$ nanocatalyst was found to be effective with respect to Arochlor 1254, with a biphenyl yield of 84.21% (Table 3).

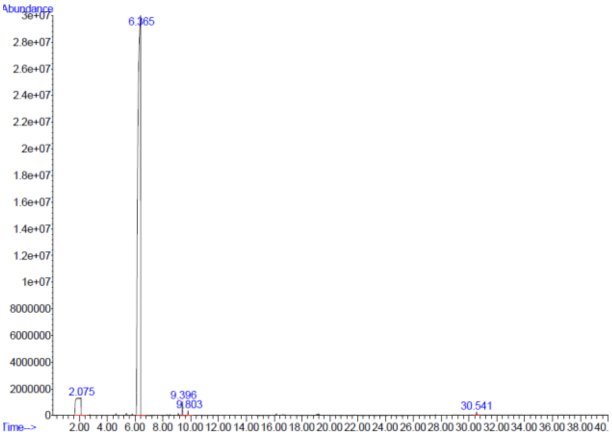


Figure 8. Chromatogram of the products of PCB hydrodechlorination – Arochlor 1254 catalyst 10Ni/AC$_m$ (10 mg) at a temperature of 25 °C

The relatively good yield of biphenyl indicates the catalytic activity of the catalyst based on nickel nanoparticles inserted on a carbon carrier. It can be assumed that a carbon carrier with a high specific surface area equal to 541.518 m^2/g allows the maximum increase in catalytic activity and possibly enhances the process of reduction of organochlorine compounds along with hydrogen, which is in good agreement with previous studies [15].

Table 3. Hydrodechlorination of PCB – Arochlor 1254 with a 10Ni/AC$_m$ catalyst (0.2 g), in a methanol medium (10 ml), at T=25 °C and P(H$_2$) = 1 atm

№	Catalyst	PCB (Arochlor 1254)	
		Product of catalysis	Conversion, %
1	10Ni/AC$_m$	Biphenyl	84,21

CONCLUSION

Thus, a 10Ni/AC$_m$ catalyst was synthesized with nanosized nickel particles (30.33–34.77 nm) inserted on a carrier, modified with hydrochloric acid activated carbon and exhibiting catalytic activity in the hydrodechlorination of Arochlor 1254 – 2,2',3,3',4-pentachlorobiphenyl under mild conditions, that is at a temperature of 25 °C and a pressure of 1 atm in methanol. Using IR spectroscopy, it was found that nickel ions in the bulk of the carrier interact with the carboxyl and carbonyl functional groups of the AC$_m$ of the carrier. The nickel nanoparticles in the 10Ni/AC$_m$ catalyst have a spherical shape and are distributed in the form of agglomerates in the volume of the carrier. It has been established that the migration of nickel nanoparticles in the bulk of the carrier forms additional channels in the form of pores, which are confirmed by the results of BET and TEM. The fixation of nickel nanoparticles in the carrier pores reduces the pore volume and increases the specific surface area of the catalyst by a factor of two compared to the AC$_m$ carrier. The developed nanocatalyst showed catalytic activity on 2,2',3,3',4-pentachlorobiphenyl. This allows to conclude that nickel nanoparticles deposited on modified highly dispersed activated carbon of the BAU-A brand have good prospects for the manufacture of highly efficient catalysts with high chemical activity with respect to persistent organic pollutants.

REFERENCES

1. Stokgol'mskaya konventsiya o stoykikh organicheskikh zagryaznitelyakh // Opublikovano vremennym sekretariatom Stokgol'mskoy konventsii o stoykikh organicheskikh zagryaznitelyakh UNEP. – 2001. – 6 maya. URL: www.un.org/ru/documents/decl_conv/conventions/pdf/pollutants (in Russian)
2. Sun B, Li Q, Zheng M, Su G, Lin S, Wu M, Li C, Wang Q, Tao Y, Dai L, Qin Y, Meng B. Recent advances in the removal of persistent organic pollutants (POPs) using multifunctional materials // Environmental Pollution. – 2020. – Vol. 265 – Part A. https://doi.org/10.1016/j.envpol.2020.114908
3. Zanaveskin L. N., Aver'yanov V. A. Nanochastitsy metallov v vodnykh rastvorakh // Zhurnal uspekhi khimii. – 2001. – T. 66, No, 2. – P. 103–116. (in Russian)
4. Gorbunova T.I., Saloutin V.I., Chupakhin O.N. Khimicheskie metody prevrashcheniy polikhlorbifenilov // Zhurnal uspekhi khimii. – 2010. – No. 79: 6. – P. 565–586. (in Russian) https://doi.org/10.1070/RC2010v079n06ABEH004047
5. Mingying D, Lizhi H, Mengyuan J, Yi Z, Jie W, Williamson G, Shuo W, Yun D, Xiaokai Z, Zhenyu W. Biochar for the Removal of Emerging Pollutants from Aquatic Systems // Int. J. Environ. Res. Public Health. – 2023. – Vol. 20. – P. 1679. https://doi.org/10.3390/ijerph20031679
6. Urbano F., Marinas J. Hydrogenolysis of organohalogen compounds over palladium supported catalysts // J. Mol. Cat. A: Chemical. – 2001. – Vol.173. – P. 329–345. https://doi.org/10.1016/S1381-1169(01)00157-1
7. Khopade A (2019). Kinetic Analysis for Low Temperature Catalytic Hydro De-chlorination of PCBs (Poly-Chlorinated Biphenyls). Master's thesis, University of Cincinnati, Ohio, USA.
8. Na H, Peijun L, Yuncheng Z, Wanxia R, Shuxiu F, Verkhozina V. Catalytic dechlorination of polychlorinated biphenyls in soil by palladium–iron bimetallic catalyst // Journal of Hazardous Materials. – 2009. – Vol. 164. – P. 126–132. https://doi.org/10.1016/j.jhazmat.2008.07.149

9. Maghami A, Gholipour-Zanjani N, Khorasheh F. A catalyzed method to remove polychlorinated biphenyls from contaminated transformer oil // Environment Science Pollution. – 2022. – Res. 29. – P. 13253–13267. https://doi.org/10.1007/s11356-021-16613-4
10. Jeon J, Yuri P, Yuhoon H. Catalytic Hydrodechlorination of 4-Chlorophenol by Palladium-Based Catalyst Supported on Alumina and Graphene Materials // Nanomaterials. – 2023. – Vol. 13. – P. 1564. https://doi.org/10.3390/nano13091564
11. Irshad B, Sayyed A, Mohamad A, Hanis Y. Decontamination of contaminated water by palladium catalyst: a short review // Natural Science Nanoscience Nanotechnology. – 2020. – Vol. 11. https://doi.org/10.1088/2043-6254/ab9c97
12. Kabdrakhmanova S, Selenova B (2021) Polychlorinated biphenyls: Environmental analytical aspects and decontamination methods [Polykhloririovannie biphenili: ekologo-analiticheskie aspekti i metodi obezvrezhivania] Berel publishing house, Ust-Kamenogorsk, Republic of Kazakhstan. ISBN 978-9965-871-76-4 (in Russian)
13. Mekhaev A.V., Pervova M.G., Taran O.P., Simakova I.L., Parmon V.N., Samorukova M.A., Boyarskiy V.P., Zhesko T.E., Saloutin V.I., Yatluk Yu.G. Zhidkofaznoe dekhlorirovanie toksichnykh tekhnogennykh produktov s ispol'zovaniem nanodispersnykh palladievykh katalizatorov na osnove sibunita // Khimiya v interesakh ustoychivogo razvitiya. – 2011. – No. 19. – P. 179–186. (in Russian)
14. Calvo L, Gilarranz M, Casas J, Mohedano A, Rodrı´guez J. Hydrodechlorination of alachlor in water using Pd, Ni and Cu catalysts supported on activated carbon // Applied Catalysis B: Environmental. – 2008. – Vol. 78. – P. 259–266. https://doi.org/10.1016/j.apcatb.2007.09.028
15. Kabdrakhmanova S, Shaimardan E, Akatan K, Selenova B, Zhilkashinova A, Erbolatuly D, Skakov M. Preparation and Characterization of the Catalyst Based on the Copper Nanoparticles // International Journal of Nanoscience and Nanotechnology. – 2022. – Vol. 18. – P. 1–10.
16. Dharitri R, Parida K. Copper and Nickel Modified MCM-41 An Efficient Catalyst for Hydrodehalogenation of Chlorobenzene at Room Temperature // Ind. Eng. Chem. Res. – 2011. –Vol. 50. – P. 2839–2849. https://doi.org/10.1021/ie101314f
17. Akatan K, Kabdrakhmanova S, Shaimardan E, Ospanova Zh, Selenova S, Toktarbay Zh. Application of X¬Ray Diffraction Method for Research of Copper Nanoparticles Obtained by Using Chemical Method // Oxidation Communications. – 2019. – Vol. 42(4). – P. 462–467. EID:2-s2.0-85081621868
18. Hyeok C, Souhail R, Shirish A, Dionysios D. Synthesis of Reactive Nano-Fe/Pd Bimetallic System-Impregnated Activated Carbon for the Simultaneous Adsorption and Dechlorination of PCBs // Chemistry of Materials. – 2008. –Vol. 20 (11). – P. 3649–3655. https://doi.org/10.1021/cm8003613
19. Kume A, Monguchi Y, Hattori K, Nagase H, Sajiki H. Pd/C-catalyzed practical degradation of PCBs at room temperature // Applied Catalysis B: Environmental. – 2008. – Vol. 81. – P. 274–282. https://doi.org/10.1016/j.apcatb.2007.12.019
20. Lokteva E. S., Golubina E. V., Antonova M. V., Klokov S. V., Maslakov K. I., Egorov A. V., Likholobov V. A. Katalizator gidrodekhlorirovaniya khlorbenzola, poluchennyy pirolizom propitannykh nitratom palladiya drevesnykh opilok // Kinetika i kataliz. – 2015. – T. 56, No. 6. – P. 753–762. (in Russian) https://doi.org/10.7868/S0453881115060106
21. Thommes M, Kaneko K, Neimark A, Olivier J, Rodriguez-Reinoso F, Rouquerol J, Sing W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report) // Pure and Applied Chemistry. – 2015. – Vol. 87 – P. 1051–1069. https://doi.org/10.1515/pac-2014-1117

ЛИТЕРАТУРА

1. Стокгольмская конвенция о стойких органических загрязнителях // Опубликовано временным секретариатом Стокгольмской конвенции о стойких органических загрязнителях UNEP. – 2001. – 6 мая. URL: www.un.org/ru/documents/decl_conv/conventions/pdf/pollutants
2. Sun B, Li Q, Zheng M, Su G, Lin S, Wu M, Li C, Wang Q, Tao Y, Dai L, Qin Y, Meng B. Recent advances in the removal of persistent organic pollutants (POPs) using multifunctional materials // Environmental Pollution. – 2020. – Vol. 265 – Part A. https://doi.org/10.1016/j.envpol.2020.114908
3. Занавескин Л. Н., Аверьянов В. А. Наночастицы металлов в водных растворах // Журнал успехи химии. – 2001. – Т. 66, № 2. – С. 103–116.
4. Горбунова Т.И., Салоутин В.И., Чупахин О.Н. Химические методы превращений полихлорбифенилов // Журнал успехи химии. – 2010. – № 79: 6. – С. 565–586. https://doi.org/10.1070/RC2010v079n06ABEH004047
5. Mingying D, Lizhi H, Mengyuan J, Yi Z, Jie W, Williamson G, Shuo W, Yun D, Xiaokai Z, Zhenyu W. Biochar for the Removal of Emerging Pollutants from Aquatic Systems // Int. J. Environ. Res. Public Health. – 2023. – Vol. 20 – P.1679. https://doi.org/10.3390/ijerph20031679
6. Urbano F., Marinas J. Hydrogenolysis of organohalogen compounds over palladium supported catalysts // J. Mol. Cat. A: Chemical. – 2001. – Vol. 173 – P. 329–345. https://doi.org/10.1016/S1381-1169(01)00157-1
7. Khopade A (2019). Kinetic Analysis for Low Temperature Catalytic Hydro De-chlorination of PCBs (Poly-Chlorinated Biphenyls). Master's thesis, University of Cincinnati, Ohio, USA.
8. Na H, Peijun L, Yuncheng Z, Wanxia R, Shuxiu F, Verkhozina V. Catalytic dechlorination of polychlorinated biphenyls in soil by palladium–iron bimetallic catalyst // Journal of Hazardous Materials. – 2009. – Vol. 164. – P. 126–132. https://doi.org/10.1016/j.jhazmat.2008.07.149
9. Maghami A, Gholipour-Zanjani N, Khorasheh F. A catalyzed method to remove polychlorinated biphenyls from contaminated transformer oil // Environment Science Pollution. – 2022. – Res. 29. – P. 13253–13267. https://doi.org/10.1007/s11356-021-16613-4
10. Jeon J, Yuri P, Yuhoon H. Catalytic Hydrodechlorination of 4-Chlorophenol by Palladium-Based Catalyst Supported on Alumina and Graphene Materials // Nanomaterials. – 2023. – Vol. 13. – P. 1564. https://doi.org/10.3390/nano13091564

11. Irshad B, Sayyed A, Mohamad A, Hanis Y. Decontamination of contaminated water by palladium catalyst: a short review // Natural Science Nanoscience Nanotechnology. – 2020. – Vol. 11. https://doi.org/10.1088/2043-6254/ab9c97
12. Кабдрахманова С., Селенова Б. Полихлорированные бифенилы: эколого-аналитические аспекты и методы обезвреживания. – Усть-Каменогорск: изд-во «Берель», 2021. – 196 с.
13. Мехаев А.В., Первова М.Г., Таран О.П., Симакова И.Л., Пармон В.Н., Саморукова М.А., Боярский В.П., Жеско Т.Е., Салоутин В.И., Ятлук Ю.Г. Жидкофазное дехлорирование токсичных техногенных продуктов с использованием нанодисперсных палладиевых катализаторов на основе сибунита // Химия в интересах устойчивого развития. – 2011. – № 19. – С. 179–186.
14. Calvo L, Gilarranz M, Casas J, Mohedano A, Rodrı´guez J. Hydrodechlorination of alachlor in water using Pd, Ni and Cu catalysts supported on activated carbon // Applied Catalysis B: Environmental. – 2008. – Vol. 78. – P. 259–266.https://doi.org/10.1016/j.apcatb.2007.09.028
15. Kabdrakhmanova S, Shaimardan E, Akatan K, Selenova B, Zhilkashinova A, Erbolatuly D, Skakov M. Preparation and Characterization of the Catalyst Based on the Copper Nanoparticles // International Journal of Nanoscience and Nanotechnology. – 2022. – Vol. 18. – P. 1–10.
16. Dharitri R, Parida K. Copper and Nickel Modified MCM-41 An Efficient Catalyst for Hydrodehalogenation of 17. Chlorobenzene at Room Temperature // Ind. Eng. Chem. Res. – 2011. –Vol. 50. – P. 2839–2849. https://doi.org/10.1021/ie101314f
17. Akatan K, Kabdrakhmanova S, Shaimardan E, Ospanova Zh, Selenova S, Toktarbay Zh. Application of X-Ray Diffraction Method for Research of Copper Nanoparticles Obtained by Using Chemical Method // Oxidation Communications. – 2019. – Vol. 42(4). – P. 462–467. EID:2-s2.0-85081621868
18. Hyeok C, Souhail R, Shirish A, Dionysios D. Synthesis of Reactive Nano-Fe/Pd Bimetallic System-Impregnated Activated Carbon for the Simultaneous Adsorption and Dechlorination of PCBs // Chemistry of Materials. – 2008. –Vol. 20 (11). – P. 3649–3655. https://doi.org/10.1021/cm8003613
19. Kume A, Monguchi Y, Hattori K, Nagase H, Sajiki H. Pd/C-catalyzed practical degradation of PCBs at room temperature // Applied Catalysis B: Environmental. – 2008. – Vol. 81. – P. 274–282. https://doi.org/10.1016/j.apcatb.2007.12.019
20. Локтева Е. С., Голубина Е. В., Антонова М. В., Клоков С. В., Маслаков К. И., Егоров А. В., Лихолобов В. А. Катализатор гидродехлорирования хлорбензола, полученный пиролизом пропитанных нитратом палладия древесных опилок // Кинетика и катализ. – 2015. – Т. 56, № 6. – С. 753–762. https://doi.org/10.7868/S0453881115060106
21. Thommes M, Kaneko K, Neimark A, Olivier J, Rodriguez-Reinoso F, Rouquerol J, Sing W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report) // Pure and Applied Chemistry. – 2015. – Vol. 87 – P. 1051–1069. https://doi.org/10.1515/pac-2014-1117

ПОЛИХЛОРЛЫ БИФЕНИЛДДІ ГИДРОДЕХЛОРЛАУҒА АРНАЛҒАН НИКЕЛЬ НАНОКАТАЛИЗАТОРЫ

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Қазіргі уақытта наноматериалдар ерекше физикалық-химиялық қасиеттеріне байланысты тиімді және селективті катализаторларды синтездеу саласындағы маңызды материалдар класына айналды. Катализатор құрамында ауыспалы металл нанобөлшектерінің болуы, полихлорбифенилдің (ПХБ) гидродехлорлану үрдісін жақсартып қана қоймай, катализатордағы асыл металл мөлшерін азайтуға мүмкіншілік береді. Тұрақты органикалық ластаушы заттарды (ТОЛ) залалсыздандыруға арналған белсенді және тұрақты гетерогенді катализаторлар алу үшін тасымалдағыш пен синтез әдісін дұрыс таңдау қажет. Зерттеуде ПХБ-ді гидродехлорлауға арналған никель нанокатализаторының синтезі ылғалды сіңіру әдісімен жүргізілді. БАУ-А техникалық белсендірілген көмір алдын ала тұз қышқылымен модификацияланып, никель катализаторын алуда тасымалдаушы (АУ$_m$) ретінде пайдаланылды. Заманауи физико-химиялық әдістерді қолдана отырып, синтезделген нанокатализатордың негізгі қасиеттері зерттелді. Модификацияланған белсендірілген көмірдегі АУ$_m$ карбоксил және карбонил топтары тасымалдаушы бойына никельді ұстап тұратын негізгі функционалды топтар екендігі ИҚ-спектроскопия әдісімен анықталды. Никель нанокатализаторының беттік құрылысы жақсы дамыған және ондағы никель нанобөлшегі тасымалдаушының микро- және мезокеуектеріне бекиді. Никель нанокатализаторы көмегімен гидродехлорлауға ұшыраған 2,2',3,3',4-пентахлоробифенилдің түрлену дәрежесі 84,21% құрайды, бұл синтезделген катализатордың ТОЛ-ға каталитикалық белсенділігін айқындайды.

Түйін сөздер: *нанокатализатор, тұрақты органикалық ластаушылар, полихлорбифенил, никель нанобөлшектері, белсендірілген көмір.*

НИКЕЛЕВЫЙ НАНОКАТАЛИЗАТОР ДЛЯ ГИДРОДЕХЛОРИРОВАНИЯ ПОЛИХЛОРБИФЕНИЛОВ

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В настоящее время наноматериалы являются важным классом материалов в области синтеза эффективных и селективных катализаторов с заданными свойствами благодаря своим уникальным физико-химическим свойствам. Наличие наноразмерных частиц переходных металлов, несомненно, улучшает протекание гидродехлорирования полихлорбифенилов (ПХБ) и позволяет снизить содержание благородного металла в катализаторе. Для получения активных и стабильных гетерогенных катализаторов обезвреживания стойких органических загрязнителей (СОЗ) необходим правильный выбор носителя и метода синтеза катализатора. В данной работе синтез никелевого нанокатализатора осуществлялся методом влажной пропитки для гидродехлорирования ПХБ. Технический активированный уголь марки БАУ-А предварительно модифицировали соляной кислотой и использовали в качестве носителя ($АУ_m$) катализатора. С использованием современных физико-химических методов исследованы основные свойства синтезированного нанокатализатора. Методом ИК-спектроскопии установлено, что карбоксильные и карбонильные группы $АУ_m$ являются основными функциональными группами, фиксирующими никель в объеме носителя. Никелевый нанокатализатор имеет развитую поверхность, на которой наночастицы никеля осаждаются в микро- и мезопорах носителя. Степень превращения 2,2',3,3',4-пентахлорбифенила составляет 84,21%, что свидетельствует о каталитической активности никелевых нанокатализаторов по отношению к СОЗ.

Ключевые слова: *нанокатализатор, стойкие органические загрязнители, полихлорбифенил, наночастицы никеля, активированный уголь.*