Int. J. Nanosci. Nanotechnol., Vol. 18, No. 1, March 2022, pp. 1-10

Preparation and Characterization of the Catalyst Based on the Copper Nanoparticles

Sana Kabdrakhmanova[1,2,*], Esbol Shaimardan[1,2], Kydyrmolla Akatan[2,3], Bagadat Selenova[1], Almira Zhilkashinova[3], Dosym Erbolatuly[3] and Mazhin Skakov[3]

[1]Satbayev University, Almaty, Kazakhstan
[2]Scientific Centre of Composite Materials, Almaty, Kazakhstan
[3]S. Amanzholov East Kazakhstan University, Ust-Kamenogorsk, Kazakhstan

(*) Corresponding author: sanaly33@mail.ru

(Received: 11 September 2020 and Accepted: 16 November 2021)

Abstract

In this paper was studied a catalytic system based on copper nanoparticles which were stabilized by polyvinylpyrrolidone (PVPD$_{40}$) and deposited on the surface of activated carbon substrate. Two methods of preparation of the catalyst were worked out: deposition on the surface and reduction in the pore volume of activated carbon. Both methods depicted the formation of copper nanoparticles, regardless of the amount of copper taken for preparation. The microstructure and dimensions of the obtained catalytic systems were investigated by using transmission electron microscopy and scanning electron microscopy. The copper nanoparticles obtained by applying to activated carbon are pure copper nanoparticles without signs of oxidation. Analysis of the surface of the catalysts showed that copper nanoparticles are concentrated in aggregates of irregular shape and layered structure. The developed catalytic systems were tested for hydrodechlorination of chlorobenzene in ethanol. The use of the developed catalyst made it possible to achieve a conversion of chlorobenzene of 94.46%. As a result of the reaction, benzene was formed as the main product. The data obtained by the chromatographic method was verified and proved by ^{1}H NMR spectroscopy.

Keywords: *Copper based catalyst, Copper nanoparticles, Hydrodechlorination of chlorobenzene, Activated carbon.*

1. INRODUCTION

Catalytic systems are widely used in almost all technologies involving organic substances. However, due to the introduction of the concept of "green chemistry", when the industry is trying to consume less organic substances that are harmful to the environment, the relevance of the catalysts usage for the neutralization of hazardous substances has only increased.

Among hazardous organic substances, organochlorine compounds occupy a special place [1]. Catalysts based on palladium on carbon carriers as well as on aluminum and silicon oxides, show the greatest activity and selectivity in the reduction reactions of chlorine-containing compounds [2-6]. However, the use of noble metals makes catalysts and the entire process of disposal of organohalogen substances expensive.

There are studies on the use of mono- and bimetallic nanoparticles of palladium, iron and nickel in reductive hydrodechlorination of organohalogen substances [3, 5, 7-9]. The optimization of the parameters of the corresponding processes was carried out depending on the type of process and the catalyst used.

In recent years, copper nanoparticles have been of greatest interest for the creation of new catalytic systems with high activity and selectivity [10-12]. In addition, copper is a relatively low toxic and cheap metal, which contributes to the production of low cost nanocatalysts. Copper nanoparticles with sizes in the range of 5-100 nm can be obtained with different reducing agents and with practically all the initial copper salts, which makes copper an attractive object for nanocatalysis.

The dimensional characteristics of copper nanoparticles are influenced by factors such as the type of reducing agent and stabilizer, temperature and reaction time as well as the concentration of the precursor. It was found that copper nanoparticles obtained by reduction with sodium borohydride in the ratios of reducing agent:precursor as 4:1 when used as a stabilizer of polyvinylpyrrolidone (PVPD) in the temperature range of 60-75 °C has a dimensional characteristic equal to about 30 nm [13]. However, the synthesized copper nanoparticles did not have proper stability in air.

A catalyst based on copper nanoparticles has been shown to be effective in reducing aromatic nitro compounds to amino compounds in the presence of tetrahydrofuran and sodium borohydride [14].

Amido-amino functionalized halloysite stabilized copper nanoparticles (aah-CuNPs) were synthesized for using by hydrazine, which was effective and stabilized in Ullmann aromatic amination reaction in DMSO [15].

The huge potential of bimetallic particles of copper and aluminum as an active reagent in the degradation of chlorinated methane derivatives has been established [16]. In this case, the reduction activity of Cu/Al bimetallic tandem in the reaction was comparable with Pd/Fe nanoparticles. In addition, recent studies have shown high catalytic activity and selectivity of copper on polyimide covalent organic framework [17] and modified phosphorus doped g-C3N4 (Cu/P-CN) [18]. A polyimide covalent organic framework (PI-COF) with high thermal and chemical stabilities was employed as an effective support for heterogeneous copper to promote the Chan–Lam coupling reaction of aryl boronic acids and amines in a mild conditions [17]. The cross-coupling between 2-aminopyridine and aryl boronic acid was implemented by photocatalyst based on copper modified phosphorus doped g-C3N4 (Cu/P-CN). In this case, the reaction with both catalysts proceeded at room temperature, is easily separated from the reaction product by simple filtration, and reused from six to eight times without significant loss in its catalytic activity and stability.

An important stage in the development of catalytic systems is the search for a catalyst support, which has a great influence on the structure and catalytic properties of the entire system. One of the most promising materials for catalysis is carbon materials. This is due to their purity, developed porous structure and high specific surface. Carbon materials are resistant to acidic and alkaline media and they also differ favorably from the point of view of the technical, economic and environmental aspects of the technology for extracting components from used catalysts [19, 20].

A carbon material for catalysis was obtained by pyrolytic compaction of soot granules with subsequent activation. The use of this catalyst in reductive hydrodechlorination reactions of toxic organic substances showed high activity in the liquid phase, in the presence of alkali and a hydrogen pressure of 1 atm [20]. Along with the advantage of subunit, there is a mesoporous structure that makes it possible to use effectively the active component when applying metal nanoparticles to the surface, the technology for producing this carrier is characterized by the implementation of a high-temperature process.

Copper catalysts carried on a carbon-containing support, obtained by pyrolysis from rice husk, are used in the decomposition of hydrogen peroxide and oxidation of cyclohexane at 40°C and atmospheric pressure [21]. A fundamentally important point in the development of catalysts for the disposal of waste from a series of organohalogen substances is the use of cheaper metals and non-deficient carriers. More promising in this direction is the use of activated carbon as a carrier [22, 23].

In this work, we obtained and studied copper catalysts carried on the activated carbon, and applied it for the reductive hydrodechlorination of chlorobenzene.

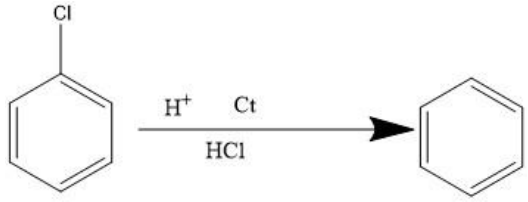

Figure 1. *Scheme of Hydrodechlorination of chlorobenzene.*

2. EXPERIMENTAL

2.1. Materials

The following reagents were used in the work: copper nitrate $Cu(NO_3)_2$ (99.9%, Sigma Aldrich), sodium tetrahydroborate $NaBH_4$ (99.9% Sigma Aldrich), polyvinylpyrrolidone (PVPD) with a molecular weight of 40,000 (Sigma Aldrich), chlorobenzene (98.80%, Russia). The listed reagents were used without further purification. A commercially available purified activated carbon of BAU-A brand was used as a carrier. Hydrochloric acid HCl (mass fraction of hydrochloric acid (HCl) 35-38%, State standard 14261-77 LLC MK "MAGNA", Russia) was used to activate the carrier.

2.2. Preparation of Catalysts

The catalysts were prepared by two methods:

Method 1

The first method is based on the classical method of producing copper nanoparticles, i.e. the synthesis was carried out by reducing copper nitrate with copper concentration of copper ions 1%, 3%, and 5% by sodium borohydride, followed by stabilization by PVPD and deposition on the activated carbon.

The preparation of Cu (1%)/C involved the interaction of copper nitrate in the amount of copper ions 1% (0.7g $Cu(NO_3)_2$) and 10 M solution of PVPD in volume ratios of 1:1 for stabilization, with further titration with a solution of sodium borohydride (0.01 M). Copper nitrate of 0.7g dissolved in 10 ml of water. The resulting solution of copper nitrate contained 1% of copper ions. Next, 10 mL of 10M PVPD solution was added to the prepared copper nitrate solution. Futher it was titrated with 0.01M of sodium borohydride.

Activated carbon was ground in an agate mortar and sieved through a brass sieve with a mesh size of 40 μm. Purification from inorganic impurities was carried out by washing with 6M of HCl solution. PVPD stabilized copper nanoparticles was deposited onto the carrier by adding 10 mL of a colloidal copper solution by intensive mixing with 0.2 g of activated carbon, where the total water pore volume was 1.6 cm^3/g, specific surface area was more than 900 m^2/g, and then separated by filtering on a Buchner funnel. The obtained precipitate was repeatedly washed with distilled water and dried at a temperature of 100 °C for 2-3 hours. 3% and 5% Cu/C catalysts were prepared by the same method, with a corresponding increase in the amount of copper nitrate.

Method 2

The second method is based on the direct production of copper nanoparticles in the pore volume of activated carbon by reduction with sodium borohydride. For this method 10 mL of solution of $Cu(NO_3)_2$, where concentration of copper ions 1% (3% and 5%) was mixed with 0.2 g of purified by 6M of HCl solution activated carbon at temperature of 50 ^{0}C and was left for sorption for 4 hours. Then 2 mL of sodium borohydride with a concentration of 0.1 M were added and left for 2 hours. Intense hydrogen evolution was observed.

The resulting precipitate was repeatedly washed with distilled water and dried at a temperature of 150 ^{0}C for 2-3 hours. After that, it was cooled at room temperature and calcinated in a muffle furnace at a temperature of 300 ^{0}C for 2 hours.

Similarly, 3% and 5% Cu/C catalysts were prepared with a corresponding increase in the amount of $Cu(NO_3)_2$.

2.3. Catalyst Characterization

The hydrodynamic diameter of copper nanoparticles was determined by dynamic laser light scattering on Malvern Zetasizer Nano ZS90 instrument (Malvern Instruments Ltd., United Kingdom). The optical properties of the obtained copper nanoparticles were studied spectroscopically (Specord 210 plus BU) in the UV-visible region. Quartz cuvettes had an optical path length of 5 and 10 mm. All measurements were carried out at 20ºC and atmospheric pressure.

The structures of the samples were studied by X-ray diffraction on X´PertPRO spectrometer (PANanalitical, Netherlands) using monochromatized copper radiation with a scan step of 0.02º. The measurement angle was 10-80º, the X-ray tube voltage was 45 kV, the current strength was 45 mA, and the measurement time at one point was 0.5 s. The diffraction indexation was performed by calculation methods and the Miller indices (h k l) of each peak were established.

The structure and morphology of the samples were studied by scanning electron microscopy (SEM) using MIRA 3 LM TESCAN electron microscope (Czech Republic). Carbon was sprayed onto the surface of the samples using magnetron sputtering of carbon fiber to increase conductivity. The measurements were carried out in high vacuum using an SE detector at an accelerating voltage of 4-20 kV.

The sizes of the nanoparticles were studied by transmission electron microscope (TEM) JEM 1011 (JEOL, Japan) completed with CCD Morada digital camera (OLYMPUS). For TEM studies, the samples were kept in ethanol, then applied to standard colloid coated copper grids. The grids were placed in a holder, which was inserted into JEM 1011 electron microscope chamber with a resolution of up to 5 nm, at an accelerating voltage of 100 kV.

FTIR analysis of chemical structures were performed on a spectrometer FTIR FT-801 (Simex, Russian), with a resolution of 1 см$^{-1}$ and a wavelength 450–4700 см$^{-1}$ according to the standard method using the standard technique with a universal attachment of a single broken total internal reflection and specular-diffuse reflection with the upper position of the sample, at a temperature of 25^{0}C. The number of scans was 100.

2.4. Hydrodechlorination of Chlorobenzene

Hydrodechlorination of chlorobenzene with synthesized catalysts was carried out according to the procedure described in [22] in a high pressure autoclave (Buchi AG).

Agilent 7890A/5975C gas chromatograph with a quadrupole mass spectrometric detector (GC/MS) was used to identify hydrodechlorination products. HP-5MS quartz capillary column (30 m x 0.25 mmi.d. x 0.25 μm) was used. The carrier gas was helium, the split ratio was 1:50, the flow rate was 1.0 cm^3/min. Temperature programming: initial 40 °C (holding for 3 min), the rate of 10°C/min to 290 °C (holding for 20 min), inlet temperature - 250 °C.

^{1}H NMR spectra were recorded on Avance III 500 MHz spectrometer (Bruker BioSpin, Germany) with an operating frequency of 500 MHz in C_6D_6 (for chlorobenzene) and DMSO-D_6 (for benzene)

3. RESULTS AND DISCUSSION

3.1. Characterization of Synthesized Nanocomposites

The microstructure of the purified activated carbon was investigated by X-ray diffraction. The obtained spectrum is shown in Figure 2. The X-ray diffraction pattern shows wide peaks at 23 ° and 43 °, corresponding to (002) and (100), respectively. This indicates a disordered amorphous structure of the material. A barely noticeable sharp peak in the region of 25 ° indicates the presence of ordered graphitized structures.

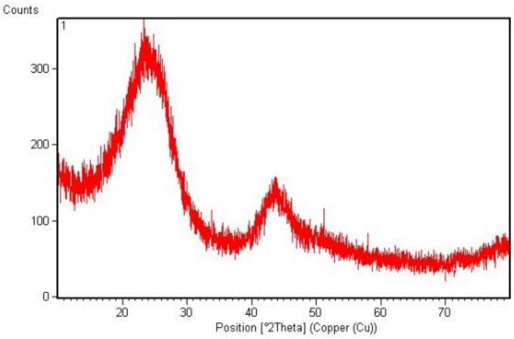

Figure 2. *XRD pattern of purified activated carbon.*

According to the SEM results, the activated carbon has a cellular-porous structure of various shapes and sizes (Figure 3). These pores are created by cross-linking between carbon walls. When the material is amplified by TEM on carbon walls, both micropores and mesopores can be detected.

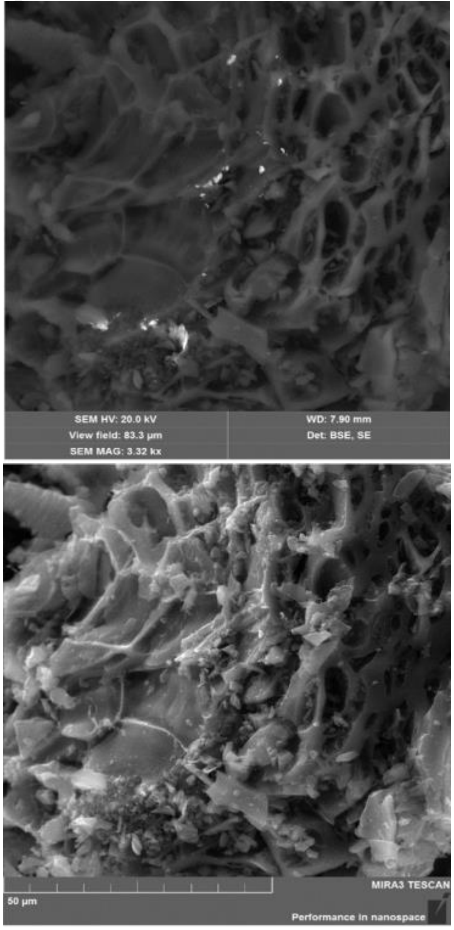

Figure 3. *SEM images of the activated carbon.*

Figure 4 shows the result of UV-vis spectroscopy. The formation of copper nanoparticles is characterized by an absorption band in the range of 500-600 nm. For spherical copper nanoparticles with a size of 2-10 nm, the position of the absorption maximum corresponds to 565-570 nm [24].

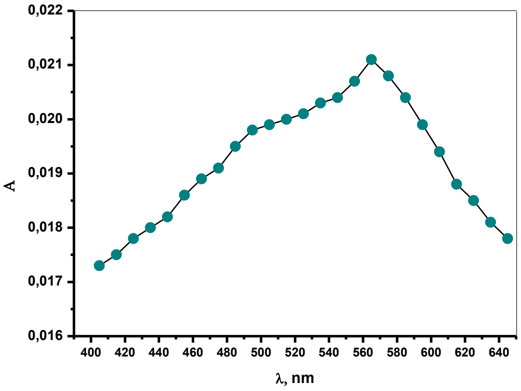

Figure 4. *Absorption spectrum of copper nanoparticles*

Figure 5 shows the numerical size distribution of copper nanoparticles obtained by dynamic light scattering. More than 80% of the nanoparticles fall into the size range of 3-4 nm. The stabilization of nanoparticles in polymers is due to the interaction of functional groups of the macromolecule with the surface of the nanoparticles. The introduction of PVPD makes the colloidal solution of metal nanoparticles stable, which is explained by the appearance in the system of finely dispersed chemically active particles of a zero-valent metal. The nitrogen and oxygen atoms in the PVPD structure form a complex with copper ions, as a result of which PVPD is adsorbed on the surface of metals and helps to stabilize nanoparticles. In Figure 5, a significant decrease in the size of copper particles after stabilization by PVPD can be observed.

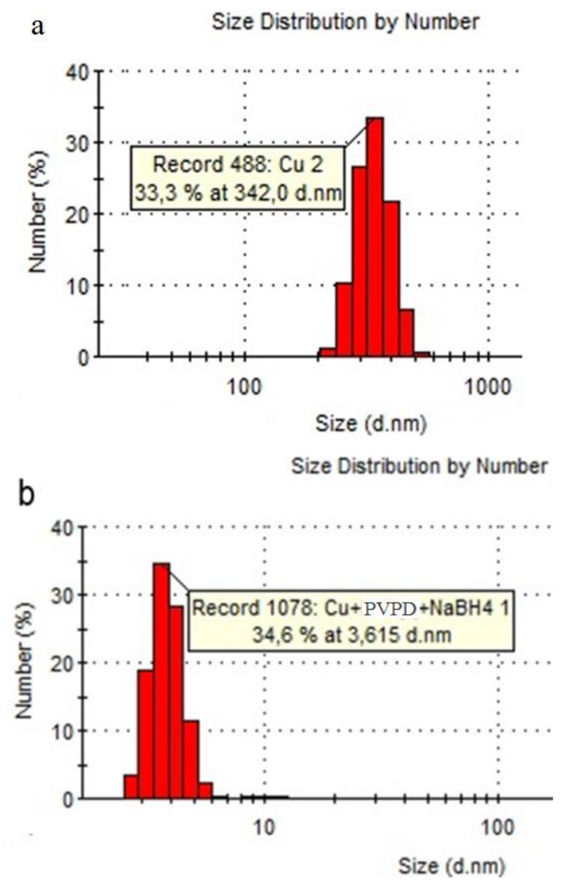

Figure 5. *Numerical size distribution of copper nanoparticles in Cu-PVPD sols: a –non-stabilized, b – PVPD stabilized.*

The catalysts were black powders consisting of a carbon matrix with copper nanoparticles dispersed in it. Figures 6 and 7 show XRD pattern of the synthesized catalyst systems.

XRD patterns are identical for both cases. The diffraction peaks (11), (200) and (220), characteristic of the crystal structure, at 2θ - 43.69, 50.88 and 72.61, respectively, were compared with the standard JCPDS copper powder diffraction map, No. 04–0836 (Figure 6) [23]. The copper nanoparticles obtained by applying to activated carbon are pure copper nanoparticles with no signs of oxidation. XRD data of the catalysts obtained by the method No. 2 showed the formation of a crystalline copper structure without an admixture of copper oxides having characteristic peaks of (111), (200) and (220) with the corresponding values of 2θ - 43.64, 50.87 and 72, 62.

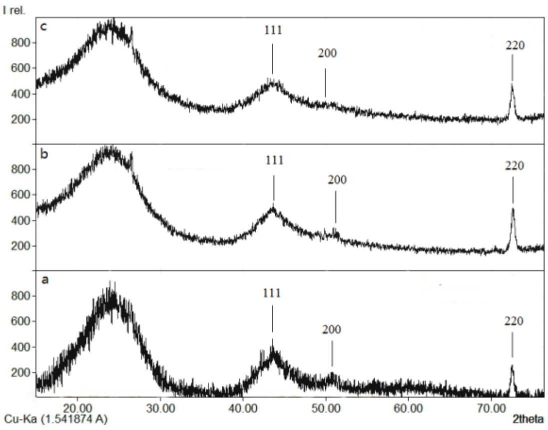

Figure 6. *XRD patterns of the catalysts prepared by Method 1: a - Cu (5%)/C, b - Cu (3%) /C; c - Cu (1%)/C [23].*

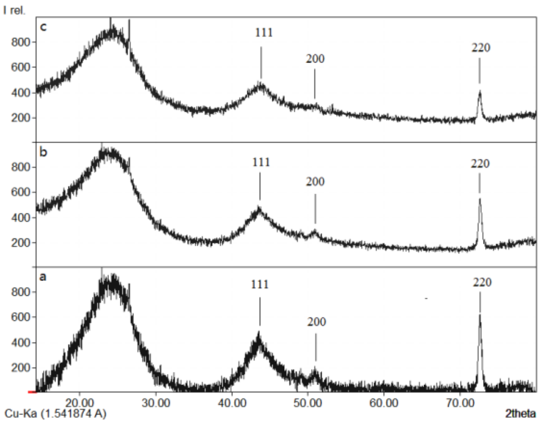

Figure7. *XRD patterns of the catalysts obtained by Method 2: a - Cu (5%)/C, b - Cu (3%)/C; c - Cu (1%)/C.*

Studies have shown the absence of any changes in particle size and crystal structure of catalyst samples depending on the amount of copper. Therefore, further studies were carried out using the catalyst with a copper content of 3%.

Analysis of the surface of the catalysts showed that copper nanoparticles deposited on the activated carbon are concentrated in irregularly shaped aggregates (Figure 8). The aggregates contain numerous formations of various shapes and sizes. These formations give a peculiar layered structure where copper nanoparticles of various shapes are found.

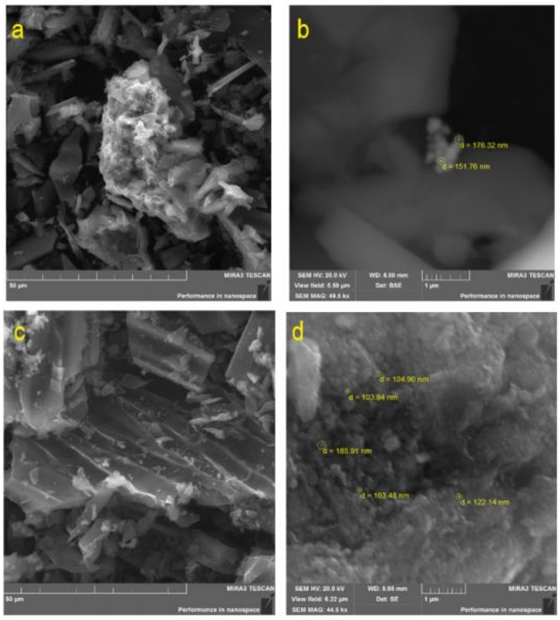

Figure 8. *SEM images of catalysts obtained by Method No. 1 (a, b) and No. 2 (c, d).*

Copper nanoparticles obtained by direct reduction of copper nitrate in the pore volume of purified activated carbon (method No. 2) are distributed relatively evenly (Figure 8, c, d). In between of relatively large aggregates, small aggregates with various sizes (103.48-185.91 nm) were recorded.

According to the TEM results, the synthesized catalysts consist of isolated copper nanoparticles, which are selectively formed on the surface layer with a thickness of up to 197.16 nm (Figure 9). The sizes of copper nanoparticles are 12.26-44.52 nm.

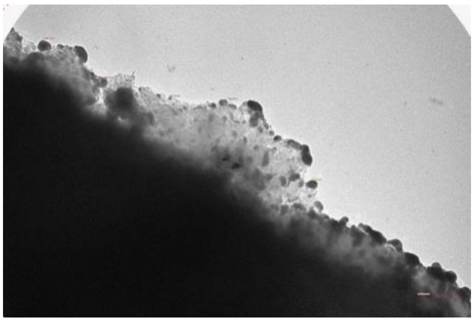

Figure 9. *TEM image of copper nanoparticles deposited on the activated carbon.*

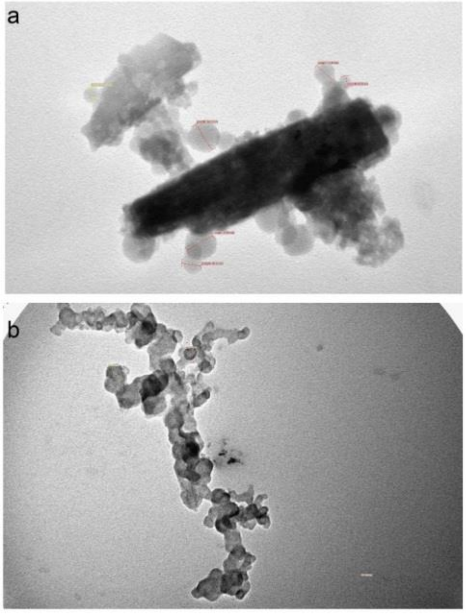

Figure 10. *TEM images of catalysts obtained by Method No. 1 (a) and No. 2 (b).*

Copper nanoparticles deposited on the activated carbon (Method No. 1) are a chain of nanoparticles located on top of each other, mainly spherical in shape. Particle sizes range from 27.28-33.11 nm and higher (Figure 10a). Copper nanoparticles obtained by reducing activated carbon in the pore volume (Method No. 2) are characterized by an isolated arrangement of clearly defined spherical nanoparticles with sizes ranging from 9.28 to 26.83 nm (Figure 10b).

Figure 11 represent the FT-IR spectrum of the studied catalyst systems. The important absorption bands are observed at 1020, 1634 and 3485 cm^{-1}. The broad and strong band that appeared at 1020 cm^{-1} may be associated with C–C stretching vibration and O–H bending vibration. The peak that appeared at 1634.84 is an indicator of water molecules that present in the nanocomposite. In addition, the O–H stretching vibration showed a broad band at around 3485 cm^{-1} [25]. Comparing the FT-IR spectra of the catalyst systems represented that there is not significant difference between them indicating the synthesis method of the catalyst.

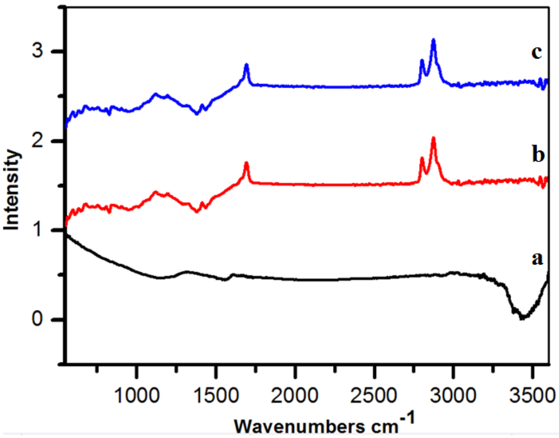

Figure 11. *FTIR spectrum of activated carbo (a)n and catalysts obtained by Method No. 1 (b) and No. 2 (c).*

In Figure 12 it can be seen from the TGA result that the main mass reduction occurs in the temperature range of 30-150 °C and 350-700 °C. The decrease in mass in the low-temperature zone, i.e. in the range of 30-150 °C, is explained by the evaporation of moisture, the release of surface and adsorption water. In the range up to 350-700 °C, there is a slight decrease in the weight of activated carbon of BAKU-A, which is achieved due to combustion of carbonaceous compounds [26].

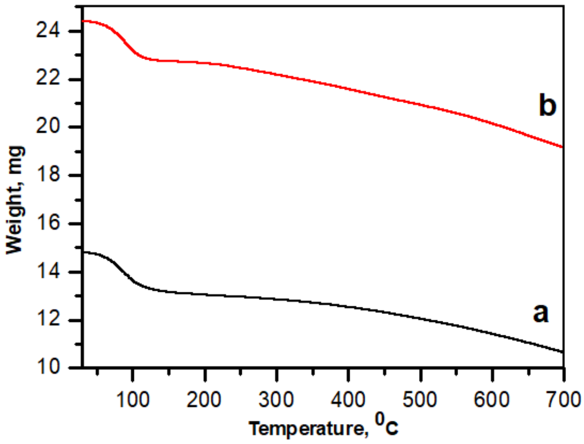

Figure 12. *TGA curves of catalysts obtained by Method No. 1 (a) and No. 2 (b).*

3.2. Hydrodechlorination of Chlorobenzene

For testing the obtained catalyst, the system obtained by the Method No. 2 with a copper content of 3% was chosen. This catalytic system was tested by hydrodechlorination of chlorobenzene in ethanol.

Studies of the initial chlorobenzene were conducted. According to the results of GC-MS analysis, the initial chlorobenzene contained 98.33% of the main component, 1.05% dichlorobenzene and 0.62% tetrachlorethylene (Figure 13a).

In the NMR spectra spectroscopy chlorobenzene (Figure 13b) there are chemical shifts in the range of 6.83-6.85 ppm, characterizing carbon atoms in positions 2 and 6, as well as shifts of 7.08-7.10 ppm characteristic of carbon in positions 1, 3, 4 and 5 of the chlorobenzene molecule.

After checking the quality of the initial chlorobenzene, it was subjected to thehydrodechlorination process with the participation of the catalyst obtained by method 2.

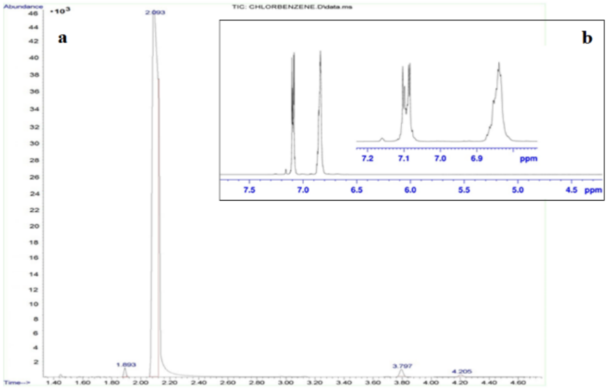

Figure 13. *Chromatogram (a) and ^{1}H NMR spectrum (b) of the initial chlorobenzene.*

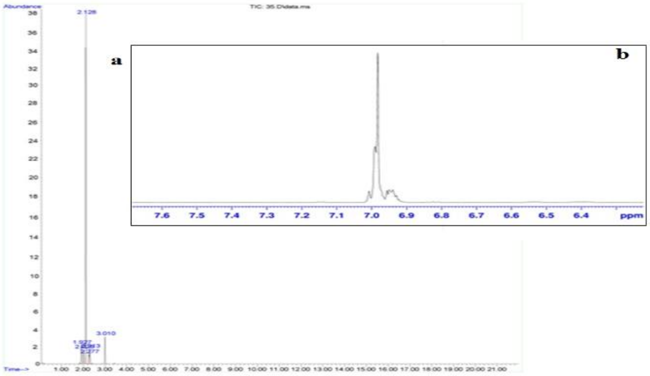

Figure 14. *Chromatogram (a) and ^{1}H NMR spectrum (b) of chlorobenzene hydrodechlorination products (catalyst – Cu (3%)/C).*

The use of the developed catalyst made it possible to achieve a conversion of chlorobenzene of 94.46%. Benzene was formed as the main product (Figure 14a). The data obtained by the chromatographic method was verified and proved by ^{1}H NMR spectroscopy.

Figure 14b shows ^{1}H NMR spectrum of the hydrodechlorination product of chlorobenzene with Cu(3%)/C catalyst system. Signal with chemical shift atδ 7.4 ppm refers to the proton of the –CH = group located in a weak field (benzene). The high rate of hydrodechlorination by the Cu(3%)/C catalytic system is due to the fact that the finely dispersed carbon support allows the catalytically active surface to be maximized, providing an increase in the yield of the reaction product.

4. CONCLUSION

Two methods of preparation of the catalyst were worked out: deposited on the surface and reduction in the pore volume of activated carbon. Both methods depicted the formation of copper nanoparticles, regardless of the amount of copper taken for preparation. Copper nanoparticles obtained by reducing in the pore volume activated carbon (Method No. 2) are characterized by an isolated arrangement of clearly defined spherical nanoparticles, the sizes of which range from 9.28 to 26.83 nm.

The developed catalytic system based on copper nanoparticles stabilized by PVPD showed a high degree of chlorobenzene conversion during catalytic hydrodechlorination. It has been established that the finely dispersed carbon support allows to increase the catalytic activity of the obtained composites due to the presence of proton donor acid groups located on the edges of the crystalline planes responsible for the hydrodechlorination reaction.

The data obtained in the study can be used in various fields of industry, from the preparation of catalysts to the production of products of the hydrodechlorination reaction of chlorine-containing substances.

ACKNOWLEDGMENT

This research has been funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. BR10965284) (2021-2023).

CONFLICT OF INTERESTS

On behalf of all authors, the corresponding author states that there is no conflict of interest.

REFERENCES

1. Tursunova, R., Kabdrahmanova, S., Selenova, B., Akatan, K., Shaimardan, Ye, Kabdrahmanova, A., “Monitoring of polychlorinated biphenyls (PCBs) in environmental objects of the city of Ust-Kamenogorsk in Kazakhstan”, *J. Ener. Proc.,* 153 (2018) 215-220.
2. Lei, C., Liang, F., Li, J., Chen, W., Huang, B., “Electrochemical reductive dechlorination of chlorinated volatile organic compounds (Cl-VOCs): effects of molecular structure on the dehalogenation reactivity and mechanisms”, *Chem. Eng. J.,* 358 (2019) 1054-1064.
3. Anaraki Firooz, A., Keyhani, M., “The Effect of Different Dopants (Cr, Mn, Cu and Ni) on ,Fe, Co Photocatalytic Properties of ZnO Nanostructures”, *Int. J. Nanosci. Nanotechnol.*, 16 (2020) 59-65.
4. Na, L., Jie, X., Xin, Y., Sun, Hao., “Distribution and formation mechanisms of polychlorinated organic by-products upon the catalytic oxidation of 1,2-dichlorobenzene with palladium-loaded catalysts”, *J. Hazard. Mater.,* 393 (2020) 122412.
5. Shen, Y., Tong, Y., Xu, J., Wang, S., Wang, J., Zeng, T., He, Yang, W., Song, S., “Ni-based layered metal-organic frameworks with palladium for electrochemical dechlorination”, *Appl. Catal. B: Env.,* 264 (2020) 118505.
6. Radkevich, V., Senko, T., Wilson, K., Grishenko, L., Zaderko, A., Diyuk, V., “The influence of surface functionalization of activated carbon on palladium dispersion and catalytic activity in hydrogen oxidation”, *Appl. Catal. A: Gen.,* 335 (2008) 241-251.
7. Balda, M., Kopinke, F., “The role of nickel traces in fine chemicals for hydrodechlorination reactions with zero-valent iron”, *Chem. Eng. J.,* 388 (2020) 124-185.

8. Zhu, K., Sun, C., Chen, H., Ali, S., Sheng, B., Xu, X., “Enhanced catalytic hydrodechlorination of 2, 4-dichlorophenoxyacetic acid by nanoscale zero valent iron with electrochemical technique using a palladium/nickel foam electrode”, *Chem. Eng. J,.* 223 (2013) 192-199.
9. Karolina, A., Śrębowata, A., Kowalewski, E., Gołąbek, K., Kostuch, A., Kruczała, K., Girman, V., Góra-Marek, K., “Nickel loaded zeolites FAU and MFI: Characterization and activity in water-phase hydrodehalogenation of TCE”, *Appl. Catal. A: Gen.,* 568 (2018) 64-75.
10. Bossola, F., Scotti, N., Somodi, F., Coduri, M., Evangelisti, C., Dal Santo, V., “Electron-poor copper nanoparticles over amorphous zirconia-silica as all-in-one catalytic sites for the methanol steam reforming”, *Appl. Catal. B: Env.,* 258 (2019) 118016.
11. Fathima, J., Pugazhendhi, A., Oves, M., Venis, R., “Synthesis of eco-friendly copper nanoparticles for augmentation of catalytic degradation of organic dyes”, *J. Mol. Liq.,* 260 (2018) 1-8.
12. Chawla, P., Kumar, N., Bains, A., Dhull, S., Kumar, M., Kaushik, R., Punia, S., “Gum arabic capped copper nanoparticles: Synthesis, characterization, and applications”, *Int. J. Biol. Macromol.,* 146 (2020) 232-242.
13. P, Rahimi., H, Hashemipour., M, Ehtesham Zadeh., S, Ghader., “Experimental Investigation on the Synthesis and Size Control of Copper Nanoparticle via Chemical Reduction Method”, *Int.l J. Nanosci Nanotechnol* 6 (2010) 144-149.
14. Souza, J., Silva, G., Fajardo, A., “Chitosan-based film supported copper nanoparticles: A potential and reusable catalyst for the reduction of aromatic nitro compounds”, *Carbohydr. Polym.,* 161 (2017) 187-196.
15. Salinas-Torres, D., Navlani-García, M., Mori, K., Kuwahara, Y., Yamashita, H., “Nitrogen-doped carbon materials as a promising platform toward the efficient catalysis for hydrogen generation”, *Appl. Catal. A: Gen.,* 571 (2019) 25-41.
16. Nidheesh, P., Khatri, J., Gandhimathi, R., Ramesh, S., “Review of zero-valent aluminium based water and wastewater treatment methods”, *Chemosphere.,* 200 (2018) 621-631.
17. Yi, Han., Mo, Zhang., Ya-Qing, Zhang., Zhan-Hui, Zhang., “Copper immobilized at a covalent organic framework: an efficient and recyclable heterogeneous catalyst for the Chan–Lam coupling reaction of aryl boronic acids and amines”, *Green Chem.,* 20 (2018) 4891–4900.
18. Jia, Q. D., Mo, Zhang., Yu-Xuan, Chen., Jin-Xin, Wang., Shan-Shan, Geng., Jia-Qi, Tang., Zhan-Hui, Zhang., “Copper anchored on phosphorus g-C3N4 as a highly efficient photocatalyst for the synthesis of N-arylpyridin-2-amines”, *Green Che.m,* 23 (2021) 1041–1049.
19. Salinas Torres, D., Navlani García, M., Mori, K., Kuwahara, Y., Yamashita, H., “Nitrogen-doped carbon materials as a promising platform toward the efficient catalysis for hydrogen generation”, *Appl. Catal. A: Gen.,* 571 (2019) 25-41.
20. Wu, B., Chen, H., Wang, S., Wai, C., Liao, W., Chiu, K., “Reductive dechlorination for remediation of polychlorinated biphenyls”, *Chemosphere,* 88 (2012) 757-768.
21. Shi, L., Zhu, P., Yang, R., Zhang, X., Yao, J., Chen, F., Gao, X., Ai, P., Tsubaki, N., “Functional rice husk as reductant and support to prepare as-burnt Cu-ZnO based catalysts applied in low-temperature methanol synthesis”, *Catal. Commun.,* 89 (2017) 1-3.
22. Akatan, K., Kabdisalim, K., Kabdrakhmanova, S., Mauletkhan, M., Ukibaev, Zh., Khabyev, A., “Synthesis of Polymer-Protected Nanoparticles of Coper on Oxide-Carbon Carrier”, *Appl. Sci. Adv. Mat. Int.,* 1 (2015) 113-117.
23. Akatan, K., Kabdrakhmanova, S., Shaimardan, E., Ospanova, Zh., Selenova, B., Toktarbay, Zh., “Application Of X-Ray Diffraction Method For Research Of Copper Nanoparticles Obtained By Using Chemical Method”, *Oxid. Commun.,* 42 (2019) 462–467.
24. Ananya Shibana, T., Jaculin, Raiza., Kannaiyan, Pandian RAHI., “Amido-Amino Clay Stabilized Copper Nanoparticles: Antimicrobial Activity and Catalytic Efficacy for Aromatic Amination”, *J. Nanosci. Nanotechnol.,* 16 (2020) 117-125.
25. Rahimi, P., Hashemipour, H., Ehtesham Zadeh, M., Ghader, S., “Experimental Investigation on the Synthesis and Size Control of Copper Nanoparticle via Chemical Reduction Method”, *Int. J. Nanosci. Nanotechnol.,* 6 (2010) 144-149.
26. Lakshmanan, S., Jostar, S., Arputhavalli, G., Jebasingh, S., Josephine, C., “'Role of Green Synthesized CuO -Nanoparticles of Trigonella FoenumGraecum LLeaves and their Impact on Structural, Optical and Antimicrobial , ”Activity, *Int. J. Nanosci. Nanotechnol.,* 17 (2021) 109-121.