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LIQUID-PHASE HYDROGENATION OF BENZENE OVER HYBRID NICKEL AND PALLADIUM NANOCATALYSTS

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The present work is devoted to the process of benzene hydrogenation to cyclohexane using nanocatalysts based on the natural mineral clinoptilolite, as well as transition metals nickel and palladium on a polymer support. Polymer-immobilized metal complexes show high efficiency and better reproducibility. Hybrid nanocomposites based on the natural mineral and metal-organic polymer complexes are expected to exhibit higher efficiency due to their polyfunctionality. Besides, the addition of the mineral clinoptilolite to the structure of the metal-polymer complex can probably improve the selectivity of the reaction, increasing the yield of the target product. In this work, the catalytic activity of catalysts of the following composition was investigated: 1) polyvinylpyrrolidone (PVP) – clinoptilolite (Kpl) (primary, decationized (DKKlp), dealuminated (DAKpl); 2) PVP-Kpl-Ni (5, 10, 15%); 3) PVP-Kpl-Pd (5, 10, 15%). It is shown that on DKKlp the yields of products, as well as the process rate, increase. On dealuminated forms of clinoptilolite, an increased rate is observed, but the catalyst activity decreases over time. On catalysts of the Ni/PVP-Kpl and Pd/PVP-Kpl compositions, better results were obtained with a metal content of 10%. Among all those studied, the catalyst based on palladium showed the highest result.

Keywords: *metal-polymer complexes, hybrid nanocomposites, polyvinylpyrrolidone (PVP), clinoptilolite (Kpl), transition metals, catalytic hydrogenation, benzene, cyclohexane.*

INTRODUCTION

The unquenchable interest of scientists in modern chemical science and industry is aimed at developing new, more effective catalytic systems with increased selectivity and the goal of obtaining more valuable products. One of the most important catalytic processes is the selective hydrogenation of benzene.

The benzene hydrogenation reaction requires highly active and selective catalysts due to the high stability of the aromatic ring. Although it is an old topic, the conversion of benzene to cyclohexane still attracts much attention because the most suitable catalyst is urgently needed for practical implementation [1].

Furthermore, taking into account low economic efficiency of a number of processes in various industries (due to high temperatures and pressures, low selectivity of catalysts used in obtaining target products), the development and advancement of new hypotheses in this direction, and, as a consequence, the synthesis of new, more efficient catalysts, is becoming an increasingly urgent task.

The hydrogenation of benzene involves six sequential hydrogen addition steps, each of which creates a C–H bond (Figure 1). Among these steps, the identity of the reactive hydrogen species at

each step and the sequence of their addition can vary depending on the local reaction environment at the catalyst surfaces. These mechanistic details at the molecular scale remain largely unknown, but such details are essential for the development of efficient catalytic processes [1-3].

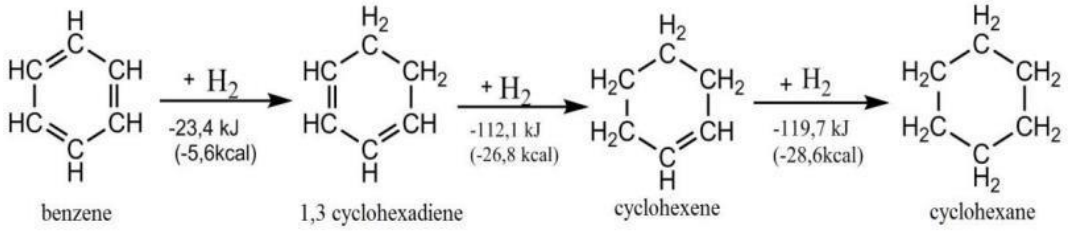


Fig. 1. Stages of benzene hydrogenation to cyclohexane [2]

In general, the benzene hydrogenation reaction is a typical heterogeneous, catalytic reaction that goes through a number of successive stages: external diffusion of benzene molecules to the catalyst surface; adsorption of hydrogen and benzene by the catalyst surface; internal diffusion of reagents in the catalyst grain; catalytic conversion on the active catalyst surface; and, finally, desorption of the reaction products (cyclohexane from the catalyst surface). The most complex process is the addition of the first pair of hydrogen atoms, which leads to disruption of the aromatic structure. Subsequent reactions proceed rapidly with increasing temperature and pressure (Figure 2). The direction of benzene hydrogenation depends on the degree of adsorption on the catalyst surface and the reaction conditions.

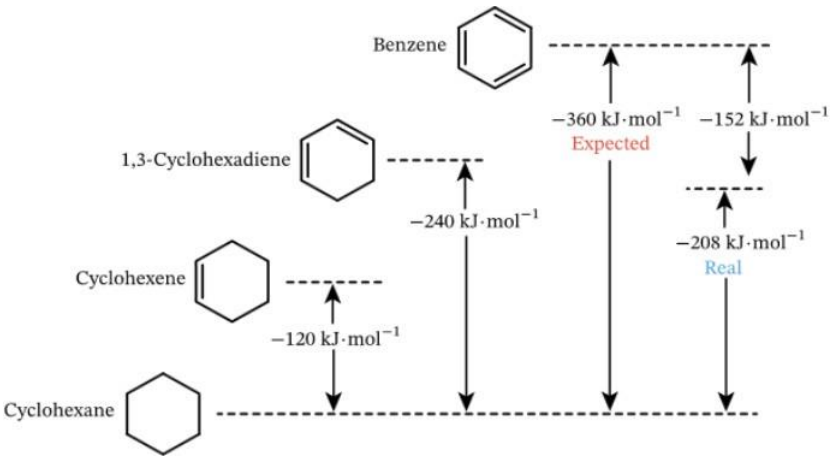


Fig. 2. Heats of hydrogenation of benzene and its derivatives [1-4]

Liquid-phase hydrogenation of benzene is shown by a scheme of three routes. If to consider benzene and cyclohexane as a hydrogenating unsaturated compound, then according to the Horiuti-rule, the proposed scheme can be a two-linear independent route. Moreover, cyclohexane is formed as a result of benzene hydrogenation, and it will also be correct if to consider that the adsorption of desorbed cyclohexane is in a new stage. The value of benzene conversion to cyclohexane shows that the reaction of selective hydrogenation of benzene occurs with the formation of cyclohexane and cyclohexene in parallel. The main task in benzene hydrogenation reactions is the choice of route [3-4].

A wide range of catalysts are used to carry out the hydrogenation reaction. The platinum group metals: platinum, palladium, rhodium and ruthenium are quite active [5]. Non-precious metals such as nickel, copper, molybdenum and cobalt are offered as economical alternatives.

It should be noted that platinum group metals, especially palladium, are considered the best catalysts, but have a significant drawback - high cost. Despite this, there are a number of works de-

voted to this group of catalysts [6-9]. Due to the high cost of palladium, it becomes necessary to develop cheaper catalysts that do not contain platinum metals. A number of studies have been carried out to compare nickel, palladium and platinum based catalysts. In this case, the attention of researchers is most often attracted by nickel catalysts [9-12], due to its availability and efficiency.

There are many known works aimed at the synthesis of hydrogenation catalysts on the base of nickel [9-12], however, in recent years, more and more studies have been conducted with bimetallic and trimetallic catalysts containing nickel.

It is worth noting that the catalytic characteristics of any catalysts depend significantly on the method of their preparation, at which it is should also take into account sulfur impurities in the catalytic system. [13]. The presence of small amounts of sulfur in the gas phase, typical for industry, creates a serious problem: sulfur will adsorb on the surfaces of transition metals and interfere with the process, changing the electronic properties of metal surfaces and destroying the ensembles of metal sections [2].

Special attention should be given to metal-polymer nanocatalysts. In this case, polymers simultaneously act as both a matrix and a stabilizer, regulating the size of metal nanoparticles during their synthesis [9, 10, 14]. The advantages of polymer carriers are confirmed in a number of studies. For example, Kompaniets et al. [14] studied the catalytic properties of palladium catalysts with the following carriers: polyaniline (PAN); PAN doped with H_2SO_4; activated carbon or aerosil (SiO_2) coated with PAN or PAN doped with H_2SO_4; PAN after heat treatment at 300°C in an H_2 atmosphere. The authors also prepared a sample by in situ polymerization of aniline in the presence of Pd^{2+}. The authors tested the catalytic activity of the catalysts using the example of the hydrogenation reaction of quinoline to 1,2,3,4-tetrahydroquinoline. The authors found that doping of PAN/H_2SO_4/C or thermal treatment of PAN before applying Pd lead to a significant increase in the catalytic activity of the composites [14]. In work [7], nanocatalysts, based on nickel immobilized on a copolymer of chitosan and polyacrylic acid, were synthesized. The synthesized catalyst was then used in the hydrogenation of benzene with a significant yield of the target product.

It is known that the combination of components with different chemical nature leads to the formation of materials with better characteristics compared to the components used separately. Such materials consisting of organic (polymer) and nanodispersed mineral phases are called "hybrid nanocomposites", "nanohybrids", "nanostructured composites", sometimes - "metal-matrix composites", "multiphase hybrids". As a rule, hybrid nanocomposites reflect the properties of synergy of the original substances, have mechanical strength, thermal stability, optimal thermal conductivity, high thermochemical, rheological, electrical and optical properties. Thus, the use of hybrid nanocomposites as selective hydrogenation catalysts is quite an urgent and important task in the modern chemical industry, which is our goal in this work.

MATERIAL AND METHODS

2.1. Synthesis of metal-polymer complexes

Nanocomposites based on polyvinylpyrrolidone (PVP) and nickel Ni (II) and palladium Pd (II) transition metals were synthesized with a metal content of 5, 10 and 15% relative to the polymer.

For the synthesis of the complexes, 1 gram of the polymer was dissolved in 25 ml of distilled water and the appropriate amount of salt was added. After stirring for 2 hours, sodium borohydride was added to the solution for reduction according to the following scheme:

$$2Ni^{2+}(aq)+BH^{-}_4(s)+2H_2O+2nPVP(aq) \rightarrow 2Ni(PVP)_n(s)+2H_2(g)+4H^{+}(aq)+BO^{-}_2(aq)$$

$$2Pd^{2+}(aq)+BH^{-}_4(s)+2H_2O+2nPVP(aq) \rightarrow 2Pd(PVP)_n(s)+2H_2(g)+4H^{+}(aq)+BO^{-}_2(aq)$$

The solution was stirred for 1 hour and washed successively with diethyl ether, acetone and distilled water, after which the precipitate was separated from the solution by centrifugation. The crosslinking agent N,N'-methylene-bis-acrylamide was added to the centrifuged part. After stirring

for some time, the samples were dried and placed under a UV lamp for crosslinking. The structures of the crosslinked metal-polymer nanocomposite samples were determined using IR spectroscopy.

2.2. Synthesis of nanohybrids based on zeolite and metal-polymer complexes

Based on the obtained metal-polymer nanocomposites, nanohybrid metal-polymer-mineral complexes were synthesized using the hydrothermal method. Zeolite clinoptilolite (Azerbaijan deposit, Aydag), pre-purified with hydrochloric acid to remove foreign impurities, was used as a natural mineral. Diffraction patterns of treated and untreated samples were obtained and compared, after which nanohybrids were synthesized.

2.3. Catalytic hydrogenation of benzene

The reaction was carried out directly in a laboratory experimental setup of a static type, in a fixed catalyst bed of a quartz reactor, at atmospheric pressure, in the temperature range of 25-80°C and at a molar ratio of C_6H_6-H_2 = 1:3. A catalyst sample of 0.8 cm^3 in volume with a grain size of 0.25-0.63 mm was placed in the reactor. The reactor was placed on a magnetic stirrer of the ―MC-5‖ brand with heating. The heating temperature was regulated by a contact thermometer. The temperature was maintained constant throughout the reactor and during the experiment.

The reagents and reaction products were analyzed by gas chromatography. The reaction products were analyzed on an Agilent 7890 B chromatograph with a 30 m HP-5 column.

Based on the obtained experimental data, the yield, selectivity and conversion were calculated using known formulas [14]:

$$\text{Conversion (X,\%)} = \frac{\text{Mole of BZ reacted}}{\text{Mole of initial BZ}} \times 100\%$$

$$\text{Selectivity (S,\%)} = \frac{\text{Mole of cyclohexane}}{\text{Mole of FAL converted}} \times 100\%$$

$$\text{Yield (\%)} = \text{Conversion} \times \text{Selectivity}$$

RESULTS AND DISCUSSION

3.1. Synthesis of metal-polymer complex

Ni-PVP complex is one of the most widely used metal-polymer complexes. This compound has important catalytic properties and useful applications in many differentbranches of industry. Whenmixingnickelchloridesalt ($NiCl_2$*$6H_2O$) andaqueousPVP solutions, nickel ions bind to the oxygen atoms of the carbonyl groups of PVP and form a Ni-PVP complex. Ni-PVP complexes have a wide range of applications due to their high strength, catalytic activity and thermal stability. It has proven itself mainly in catalytic processes. Their catalytic efficiency is explained by the stability of nickel in the active state and the even distribution of nickel ions in the polymer matrix. Part of the structure of the Ni-PVP complex is shown below (Figure 3).

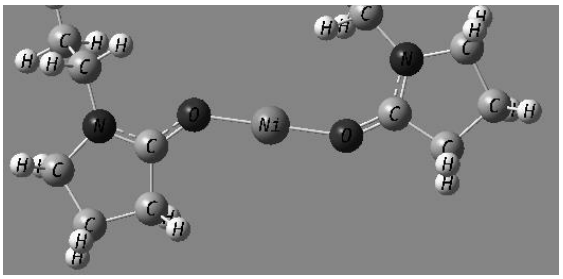
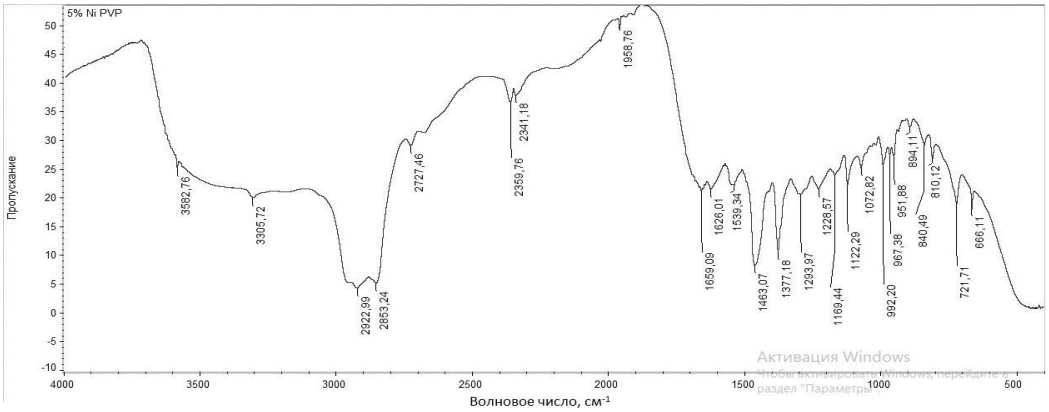


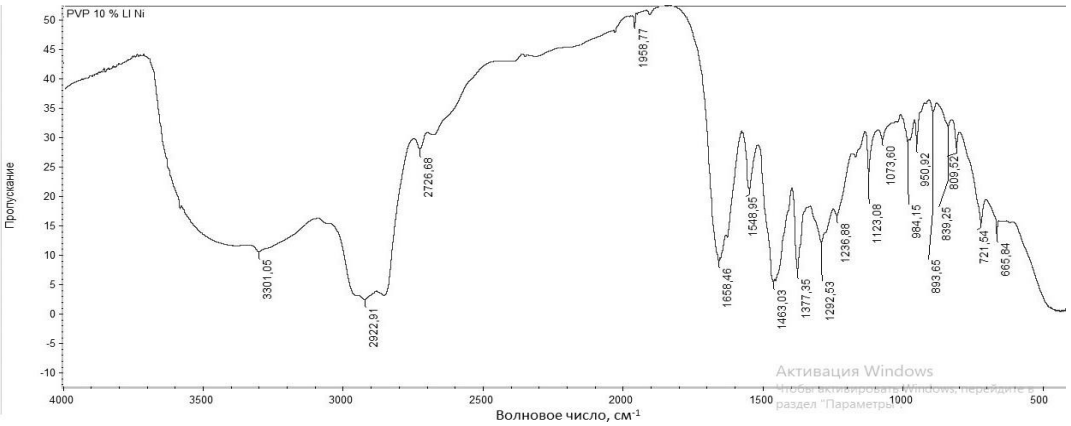
Fig. 3. The structure of Ni-PVP complexes

Based on the IR spectra presented below (Figure 4), the SEM study of metal-containing polymers showed that the characteristic peak of C=O interaction becomes asymmetric after the addition of a metal salt, which is a clear example of a strong polymer-metal bond. The IR spectra at 3454

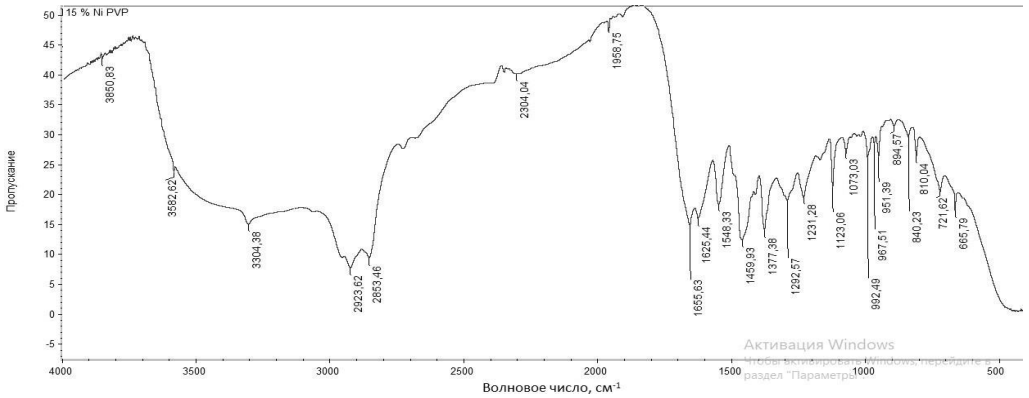
and 3407 cm^{-1} of the polymer itself and the metal-containing samples show absorption bands characteristic of each sample. The absorption band characteristic for the carbonyl group of the polymer is located at 1655 cm^{-1} in the lactane ring, which is expanded due to the C=N double bond. In the metal-polymer complex, this absorption band shifted to 1651 cm^{-1}. The observed difference in the IR spectra of the polymer and the metal-polymer complex indicates a strong donor-acceptor interaction between the oxygen atom and the metal ions in the polymer ligand.



Ia



Ib



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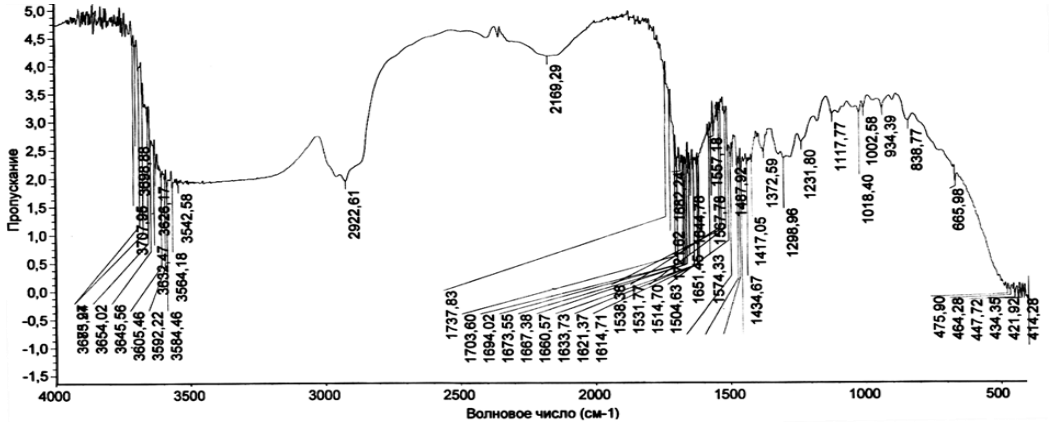

Fig. 4. IR spectra of synthesized metal-polymer complexes: Ni 5% - PVP (I a), Ni 10% - PVP (I b), Ni 15% - PVP (I c); Pd – PVP (II).

Part of the Pd-PVP structure is presented as follows (Figure 5).

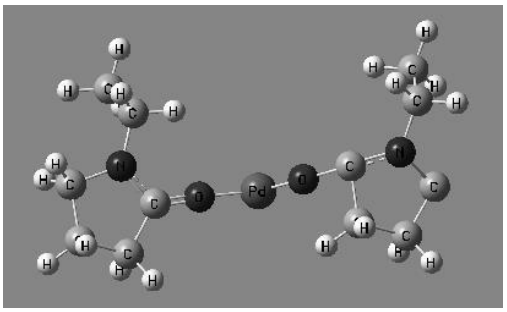

Fig. 5. The structure of Pd-PVP complexes

3.2. Synthesis of nanohybrids based on zeolite and metal-polymer complexes

Clinoptilolite, which is used as a mineral, has a complex formula: (Na, K, Ca)2-3Al3(Al, Si)2Si13O36 •12H2O and has ion-exchange properties, so it is of great interest to scientists. At the first stage of the research, purification and confirmation of the structure of this mineral was carried out. Based on X-ray diffraction, it was found that the percentage of crystallinity of the purified substance (Figure 6) increased compared to the original sample.

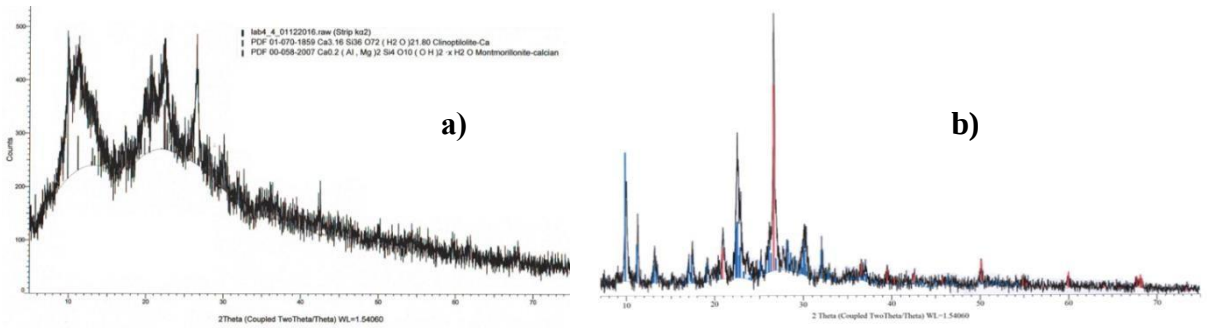

Fig. 6. Diffraction pattern of the original (a) and purified (b) clinoptilolite

Metal-polymer nanocomposites with clinoptilolite were obtained by hydrothermal synthesis. The diffraction patterns of the obtained products (Ni-PVP-clinoptilolite, Pd-PVP-clinoptilolite) are presented below (Figure 7).

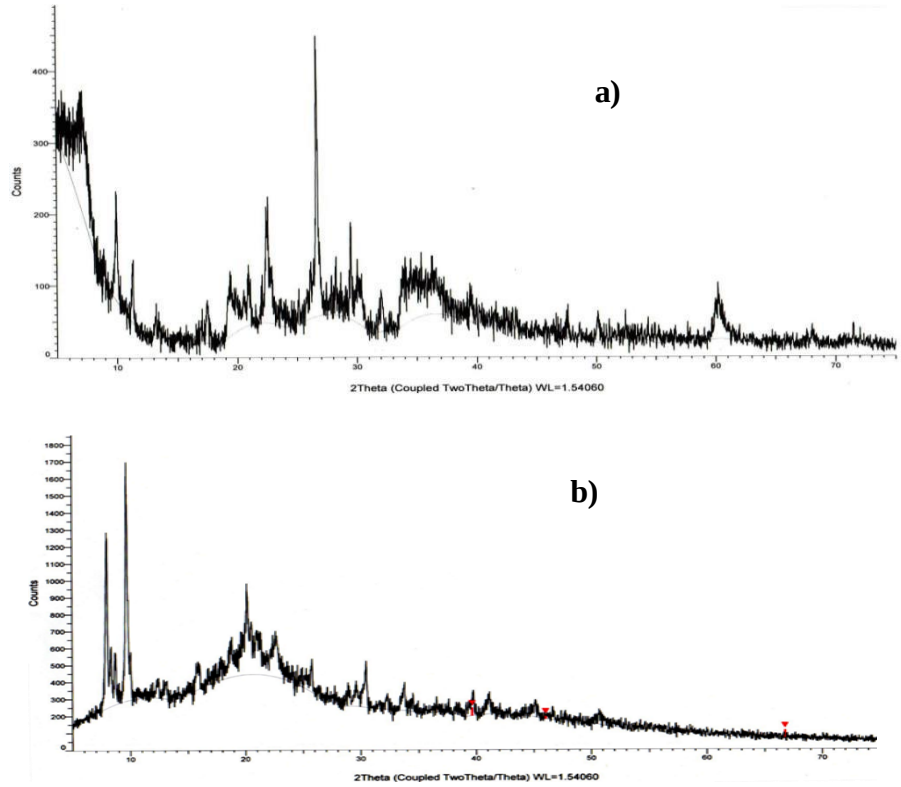

Fig. 7. Diffraction patterns of Ni-PVP-clinoptilolite (a) and Pd-PVP-clinoptilolite (b) complexes

As can be seen from the Figure 7, after construction we observe an increase in the crystalline phase and the production of a system with a more regular structure.

Based on research, it is believed that metal-polymer-mineral complexes have a number of properties that allow them to act as more effective catalysts and adsorbents in various chemical processes.

3.3. Carrying out the process of catalytic hydrogenation of benzene

As a result of the conducted research, it was found that the catalytic activity of the obtained catalyst samples in the studied reaction significantly depends on the properties and structure of metals, polymer, and zeolite, on the reaction conditions (temperature, etc.) as well.

It has been establishedthat the effect of the obtained metal/polymer-mineral nanocatalysts on the benzene conversion reaction proceeds in the following direction: hydrogenation of benzene; formation of carbonyl compounds. The yield of the reaction product is influenced by the nature of the metals, the properties of the polymerand the porousstructure of the zeolite, the physical and chemical composition, and the reaction conditions.

The results of researchcarried out on benzene hydrogenation on other catalysts showed that depending on various factors, such as polymer properties, structural properties, as well as the type of zeolite, and reaction conditions. As a result of the reaction, along with the target product - cyclohexane, cyclohexadiene and cyclohexene compounds are formed.

In order to determine the nature of the influence of the structural properties of the polymer and zeolite on the benzene hydrogenation reaction, the initial catalytic activity of polyvinylpyrrolidone and primary zeolite in the benzene hydrogenation reaction was studied, the results obtained are presented in Table 1. The Table shows the results of experiments on primary alkaline and alkaline earth cationic forms of zeolite.

Porous zeolites are characterized by a small internal surface area (8.0–20.0 m^2/g) and small pores (4.2–4.9 Å). These types of zeolites help in the selective conversion of benzene to cyclohexane in the benzene hydrogenation reaction. It is known from Table 1 that among the ionic structures of porous zeolite, the yield of cyclohexane is higher in dealuminated clinoptilolites. 15.8% cyclohexane is obtained with a selectivity of 76.7% on dealuminated clinoptilolite zeolite at temperature of 50°C and a molar ratio of benzene to H_2 = 1:3.

Table 1.

Hydrogenation of benzene on nanocatalysts based on polyvinylpyrrolidone and clinoptilolite (T=50°C, benzene-H_2=1:3, τ=6 h)

Catalyst	X, %	S, %	Yield of reaction product, %	
			C_6H_{10}	C_6H_{12}
Polyvinylpyrrolidone	—	—	—	—
Clinoptilolite	11.5	16.5	9.6	1.9
PVP/5%Clp	15.3	18.3	12.5	2.8
PVP/5%DCClp	17.7	63.8	6.4	11.3
PVP/5%DAClp	20.6	76.7	4.8	15.8

X - benzene conversion; S - process selectivity with respect to cyclohexane; DCClp - decationized clinoptilolite; DAClp - dealuminated clinoptilolite

In many processes of heterogeneous hydrogenation, the activation of hydrocarbon molecules by their dissociative adsorption with the participation of the main centers is considered a weakstage.Active centers play the role of the maincenter,formedon the surface of the catalyst.A review of the catalytic properties of PVP/Clp and PVP/DCClp shows that these catalysts are characterized by low selectivity and low activity in the reaction of partial hydrogenation of benzene. Decationization of zeolites leads to an increase in the specific surface area, the size of the inlet windows and the number of Brønsted acid centers of the catalyst, which, in addition to hydrogenation reactions, exhibit activity in processes of acid-base type, especially in the disproportionation of intermediate products of benzene hydrogenation. Decationized zeolite samples are obtained by treating primary Na-forms with 10% aqueous solution of NH_4Cl or 2% solution of HCl, followed by washing to remove chloride ions, drying at 110–120°C and calcination at 500–550°C for 5 hours. Figure 8 shows that higher yields of hydrogenation products were obtained on decationized natural clinoptilolite than on the initial clinoptilolite sample, which is caused by the mixture of Me^{n+} ions. An increase in the degree of decationization leads to an increase in the rate of benzene hydrogenation reaction.

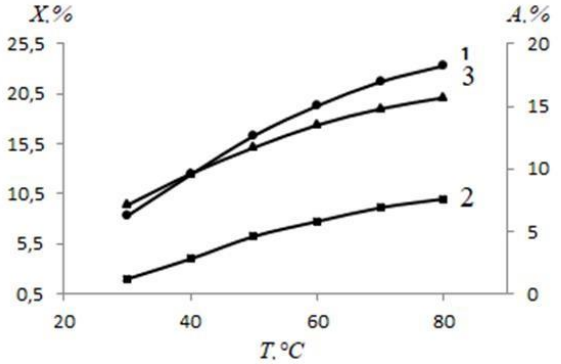

Fig. 8. Temperature dependence of benzene conversion (1) and the yield of reaction products: cyclohexene (2) and cyclohexane (3) (A). (benzene-H_2=1:3; PVP/5%DCClp).

Further studies were carried out on dealuminated forms of zeolite for a detailed analysis of the reaction results (Figure 9).

Due to the inclusion of dealuminated forms of zeolite in the composition of known hydrogenation catalysts, the rate of the hydrogenation process increases and higher results are achieved. A study of the dynamics of the rate of formation of benzene hydrogenation products shows that their activity decreases rapidly with time, and the selectivity of the reaction for unsaturated and saturated hydrocarbons exceeds the maximum.

Catalytic systems obtained on dealuminated forms of clinoptilolite have high selectivity in the benzene hydrogenation reaction.

The optimal ratio of components in the indicated catalytic systems was found by keeping the amount of one of the substances constant and changing the amount of the other one.

As a result of the conducted research, a nanocomposite containing natural dealuminated zeolite clinoptilolite and synthetic polymer polyvinylpyrrolidone in various mass quantities was synthesized as an effective catalyst for selective hydrogenation of benzene to cyclohexane. The optimal mass fraction of clinoptilolite (5%) included into the catalyst composition and optimal reaction conditions (T = 50°C, C_6H_6-H_2 = 1: 3) were selected. The yield of cyclohexane was 15.8%, the conversion of benzene was 20.6% and the selectivity was 76.7%.

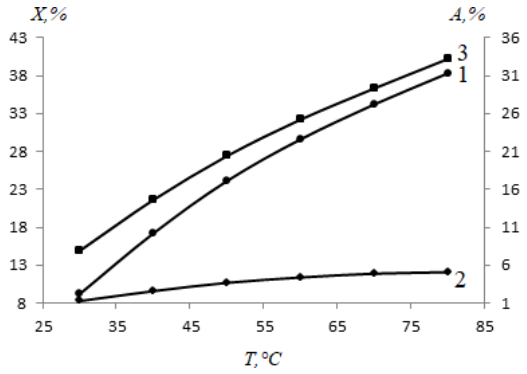

Fig. 9. Temperature dependence of benzene conversion (1) and the yield of reaction products: cyclohexene (2) and cyclohexane (3) (A, %). (C_6H_6-H_2=1:3; PVP/5%DAClp)

In addition, the catalytic properties of the synthesized metal-containing catalysts were studied in the selected reaction. The results obtained are presented in Table 2.

Table 2.

Hydrogenation of benzene on nanocatalysts based on Ni/polyvinylpyrrolidone-clinoptilolite (T=50°C, C_6H_6- H_2=1:3, τ=6 hours)

Catalyst	X, %	S, %	Yield of the reaction product, %	
			C_6H_{10}	C_6H_{12}
5%Ni/PVP-Clp	29.5	65.7	10.1	19.4
10%Ni/PVP-Clp	37.9	67.5	12.3	25.6
15%Ni/PVP-Clp	21.5	61.4	8.3	13.2

X - benzene conversion; S - process selectivity with respect to cyclohexane

As can be seen from the Table 2, 25.6% of cyclohexane is obtained with a selectivity of 67.5% with respect to the Me/PVP-clinoptilolite catalyst containing 10% Ni at 50°C and a molar ratio of C_6H_6–H_2=1:3. At that time, the conversion was 37.9%.

Analyzing the results obtained in the course of the benzene hydrogenation reaction carried out on the Pd/PVP-clinoptilolite catalyst, it was found that, unlike the nanocatalyst containing metallic Ni, the sample of the nanocatalyst containing Pd showed a higher result in the selected object. Thus,

on the Me/PVP-Clinoptilolite catalyst containing 10% Pd at temperature of 50°C and a molar ratio of C_6H_6-H_2=1:3, 34.3% cyclohexane is obtained with a selectivity of 69.8%. This time, the conversion was 49.1% (Table 3).

Table 3.

Hydrogenation of benzene on nanocatalysts based on Pd/PVP-clinoptilolite
(T=50°C, C_6H_6-H_2=1:3, τ=6 hours)

Catalyst	X, %	S, %	Yield of the reaction product, %	
			C_6H_{10}	C_6H_{12}
5%Pd/PVP-Clp	37.3	66.2	12.6	24.7
10%Pd/PVP-Clp	49.1	69.8	14.8	34.3
15%Pd/PVP-Clp	25.7	63.4	9.4	16.3

X - benzene conversion; S - process selectivity with respect to cyclohexane

However, the activity of catalysts in the working process decreases over time, which is associated with a change in the phase composition and coking of the catalyst surface. All systems exhibit activity in reactions of mild, destructive and deep hydrogenation.

CONCLUSION

The work investigated the catalytic activity of hybrid nanocomposites based on a natural mineral and organometallic polymer complexes in the catalytic hydrogenation of benzene to cyclohexane. The catalysts studied were: 2) PVP – Kpl (primary, decationized, dealuminated); 3) PVP-Kpl-Pd (5, 10, 15%). As a result of the carried out experiments it was established, that the yield of cyclohexane in the considered reaction of benzene hydrogenation with participation ofpolyvinylpyrrolidone and clinoptilolite with silicate module SiO_2/Al_2O_3=8.68 at temperature of 50°C, with a molar ratio of C_6H_6-H_2=1:3 was 15.8%, the selectivity of the process for the target product was 20%, benzene was 76.7% at conversion of 0.6%, 25.6%, 37.9% and 67.5% in PVP/Clp containing 10% Ni^0. On the PVP/Clp nanocatalyst containing 10% Pd, these values were 34.3%, 49.1% and 69.8%. Moreover, after the regeneration process of the synthesized catalysts due to coking, the catalysts were retested and a repetition of the initially obtained results was observed. This is anapparent indicator of the efficiency and effectiveness of the synthesized catalysts. In the future metal-saving ultra-dispersed nanocatalysts on a polymer-mineral base can be studied in other chemical processes (oxidation, hydrogenation, oxidative dehydrogenation).

REFERENCES

1. R. Bakri. D. Agus. L. Mardiana, D. O. Apriandanu. Influence of Ni concentration on α-MnO2 catalyst support and its potential application for benzene hydrogenation to cyclohexane//- Kuwait City:Kuwait Journ. Sci. – 2025, 52 (1), – 100288.
2. H. Cai. H. Nie. Z. Lu. C. V. Singh и Y.-H. Chin (Cathy). Catalytic consequences of the identity and coverages of reactive intermediates during benzene hydrogenation on Pt. Pd. and Pt-Re catalysts // - Amsterdam: Journ. Catal. – 2024, 436, 115582.
3. V. M. Lin S.D. Hydrogenation of Aromatic Hydrocarbons over Supported Pt Catalysts I. Benzene Hydrogenation //- Amsterdam: Journ. Catal. -1993, 143 (2), - p. 539-553.
4. N. Shikhverdieva. U. Mammedova и N. Zeynalov. The scientific basis of industrial application of the process of selective hydrogenation of benzene in different catalytic systems // -Baku: Azerb. Chem. Journ. – 2023, 3, - p. 39-52.
5. K. Thomas. C. Binet. T. Chevreau и et al. Hydrogenation of Toluene over Supported Pt and Pd Catalysts: Influence of Structural Factors on the Sulfur Tolerance// - Amsterdam: Journ. Catal. – 2002, 212 (1), - p. 63-75.

6. R. Suleymanova. N. Zeynalov. L. Qulubayova et al. Study of the liquid-phase hydrogenation of benzene in the presence of metal-polymer complexes based on polyvinylpyridines// - Baku:Azerb. Chem. Journ. – 2023, 2, p. 97-103.
7. S. Jackson. Hydrogenation: Catalysts and Processes. Berlin. Germany: Walter de Gruyter, - 2018.
8. L. Simon. J. V. Ommen. A. Jentys, J. Lercher. Sulfur-Tolerant Pt-Supported Zeolite Catalysts for Benzene Hydrogenation: I. Influence of the Support // - Amsterdam: Journ. Catal. - 2001, 201 (1), p. 60-69.
9. O. Belskaya. R. Mironenko. T. Gulyaeva et al. Catalysts Derived from Nickel-Containing Layered Double Hydroxides for Aqueous-Phase Furfural Hydrogenation //- Basel: Catal. – 2022, 12, - p. 598-615.
10. Z. Abdelsadek. J. Holgado. D. Halliche et al. Examination of the deactivation cycle of NiAl- and NiMgAl-hydrotalcite derived catalysts in the dry reforming of methane //- Dordrecht:Catal. Lett, – 2021, 151, - p. 2696–2715.
11. Y. Zhan. K. Song. Z. Shi et al. Influence of reduction temperature on Ni particle size and catalytic performance of Ni/Mg(Al)O catalyst for CO_2 reforming of CH_4 //- Amsterdam – 2020, Int. J. Hydrog. Energy, 45, - p. 2794–2807.
12. P. Mierczynski. M. Mosinska. N. Stepinska et al. Effect of the support composition on catalytic and physicochemical properties of Ni catalysts in oxy-steam reforming of methane //- Amsterdam: Catal. Today – 2021, 364, - p. 46–60.
13. Y. Gao. W. Yi. J. Yang. K. Jiang et al. Effect of Calcination Atmosphere on the Performance of Cu/Al2O3 Catalyst for the Selective Hydrogenation of Furfural to Furfuryl Alcohol //- Basel: Molecules, - 2024, 29 (12), - p. 2753-2767.
14. O. Kompaniiets. V. Subotin. A. Poturai et al. Catalytic Properties of Pd Deposited on Polyaniline in the Hydrogenation of Quinoline // - Basel: Chemistry – 2024, 6, - p. 738-759.

BENZOLUN HİBRİD NİKEL VƏ PALLADİUM NANOKATALİZATLARI ÜZƏRİNDƏ MAYE FAZASINDA HİDROGENLƏŞDİRİLMƏSİ

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Hazırkı iş benzolun tsikloheksana hidrogenləşdirilməsi prosesinə həsr olunmuşdur. Prosesdə təbii mineral olan klinoptilolitə və polimer əsaslı keçid metallarına – nikel və palladiuma əsaslanan nanokatalizatorlardan istifadə olunmuşdur. Polimerə immobilizə olunmuş metal kompleksləri yüksək effektivlik və daha yaxşı reproduktivlik nümayiş etdirir. Təbii mineral və metal-polimer komplekslərinə əsaslanan hibrid nanokompozitlərin çoxfunksiyalılığı səbəbindən daha yüksək katalitik aktivlik göstərəcəyi gözlənilir. Bundan əlavə, metal-polimer kompleksinin quruluşuna klinoptilolit mineralının əlavə olunması reaksiyanın selektivliyini artıraraq hədəf məhsulun çıxımını yaxşılaşdıra bilər.Bu işdə aşağıdakı tərkibə malik katalizatorların katalitik aktivliyi araşdırılmışdır: polivinilpirrolidon (PVP) – klinoptilolit (Kpl) (ilkin, de-kationlaşdırılmış (DKKpl), de-alüminləşdirilmiş (DAKpl));PVP-Kpl-Ni (5, 10, 15%);PVP-Kpl-Pd (5, 10, 15%). Tədqiqat göstərmişdir ki, DKKpl üzərində həm məhsulun çıxımı, həm də prosesin sürəti artır. De-alüminləşdirilmiş klinoptilolit formalarında sürətin artması müşahidə olunur, lakin zaman keçdikcə katalizatorun aktivliyi azalır. Ni/PVP-Kpl və Pd/PVP-Kpl tərkibli katalizatorlarda isə metalın 10%-lik miqdarında daha yaxşı nəticələr əldə edilmişdir. Tədqiq olunan bütün nümunələr arasında ən yüksək nəticə palladium əsaslı katalizator tərəfindən göstərilmişdir.

Açar sözlər: *metal-polimer kompleksləri, hibrid nanokompozitlər, polivinilpirolidon (PVP), klinoptilolit (Kpl), keçid metalları, katalitik hidrogenləşmə, benzol, tsikloheksan.*

ЖИДКОФАЗНОЕ ГИДРИРОВАНИЕ БЕНЗОЛА НА ГИБРИДНЫХ НИКЕЛЕВЫХ И ПАЛЛАДИЕВЫХ НАНОКАТАЛИЗАТОРАХ

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Настоящая работа посвящена исследованию процесса гидрирования бензола в циклогексан с использованием нанокатализаторов на основе природного минерала клиноптилолита, а также переходных металлов никеля и палладия на полимерном носителе. Полимерно-иммобилизованные металлокомплексы демонстрируют высокую эффективность и лучшую воспроизводимость. Ожидается, что гибридные нанокомпозиты на основе природного минерала и металлорганических полимерных комплексов будут проявлять более высокую эффективность благодаря их полифункциональности. Кроме того, добавление минерала клиноптилолита в структуру металлполимерного комплекса, вероятно, может повысить селективность реакции, увеличивая выход целевого продукта. В работе исследована активность катализаторов следующего состава: 1) поливинилпирролидон (ПВП) – клиноптилолит (КПл) (первичный, декатионированный (ДККПлп), деалюминированный (ДАКПл); 2) ПВП-КПл-Ni (5, 10, 15%); 3) PVP-Kpl-Pd (5, 10, 15%). Показано, что на DKKlp выходы продуктов, а также скорость процесса увеличиваются. На деалюминированных формах клиноптилолита наблюдается увеличение скорости, однако активность катализатора снижается со временем. На катализаторах составов Ni/PVP-Kpl и Pd/PVP-Kpl лучшие результаты получены при содержании металла 10%. Среди всех исследованных катализатор на основе палладия показал наивысший результат.

Ключевые слова: *металлополимерные комплексы, гибридные нанокомпозиты, поливинилпирролидон (ПВП), клиноптилолит (КПл), переходные металлы, каталитическое гидрирование, бензол, циклогексан.*