



Article Preparation of Nanoporous Carbon from Rice Husk with Improved Textural Characteristics for Hydrogen Sorption

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Abstract: This study proposes a method to control the pore-forming process by performing preliminary mechanical activation of the initial rice husk before carbonization. Preliminary mechanical activation of the initial rice husk leads to the loosening of the intercellular substance and its partial depolymerization, thereby increasing the availability of its internal structure for pore formation during carbonization and chemical activation. Using the method described above, nanoporous carbon was obtained with a Brunauer–Emmett–Teller (BET)-calculated specific surface area of 2713 m²/g, a micropore specific surface area calculated by using the Dubinina–Radushkevich (D-R) method of $3099 \text{ m}^2/\text{g}$, and a total pore volume calculated by using the Barett–Joyner–Halenda (BJH) method of $1.625 \text{ cm}^3/\text{g}$. Due to these characteristics, the adsorption capacity in the obtained sample was for hydrogen 3.7 wt.% at a temperature of $-190 \,^{\circ}\text{C}$ and a pressure of 9 kgf/cm², which is 29.7% higher than the adsorption capacity of nanoporous carbon obtained based on rice husk without mechanical activation. The composite "carbon–platinum" NC-2/Pt_{10%}, at a temperature of 20 °C and a pressure of 9 kgf/cm², showed an increase in sorption capacity of 27% compared to pure nanoporous carbon NC-2, which is explained by the emergence of the spillover effect.

Keywords: mechano-activation; nanoporous; carbon; adsorption; hydrogen storage; spillover effect

1. Introduction

The beginning of the 21st century was marked by the active implementation of environmental programs by industrialized countries to reduce CO₂ emissions into the atmosphere, and after the signing of the Paris Agreement in 2015 under the United Nations Framework Convention on Climate Change, hydrogen was seen as a viable alternative to hydrocarbon fuels [1]. In recent decades, there has been an increased interest in hydrogen as a fuel and energy carrier, the reserves of which are virtually unlimited. Hydrogen is a universal type of energy resource, it can be used as a fuel for energy production in different types of operating cycles and as an energy carrier for transportation in gaseous, liquid, and bound states. With the help of hydrogen, it is possible to store energy, and among other types of organic fuel, hydrogen has the highest calorific value per unit mass and the least negative impact on the environment.

The full cycle of hydrogen energy includes four stages: production, storage, transportation, and use of hydrogen as an energy carrier. One of the key industries consuming hydrogen as a fuel is the motor vehicle industry. The widespread adoption of hydrogen as a vehicle fuel is critically dependent on the ability to store hydrogen onboard at high volumetric and gravimetric densities, as well as the ability to extract/inject it at a sufficiently high rate. Some of the promising materials that meet these requirements are substances capable of accumulating hydrogen through the process of physical adsorption, which is



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). characterized by the lowest strength of hydrogen bonding with the surface. The rapid development of nanotechnology opens up the possibility of creating hydrogen storage systems based on nanoporous solid carriers capable of accumulating hydrogen through the process of physical adsorption. In physical adsorption, gaseous hydrogen is sorbed on the adsorbent surface due to van der Waals forces, which are weak (1–10 kJ/mol), and above the critical temperature, sorption can occur at a depth of not more than one monolayer. In this regard, the materials used for hydrogen storage through the physical adsorption process should have a high specific surface area. The review articles [2–7] present research in the field of hydrogen storage based on porous materials and present major advances in the development of the use of porous materials in sustainable hydrogen-storage technologies.

One of the promising materials for hydrogen storage as an adsorbent is nanoporous carbon derived from plant raw materials. This type of carbon boasts a high specific surface area, a stable framework structure, mass productivity, and rapid kinetics in its adsorption/desorption processes. Reviews [8-13] have discussed the fundamental role of binding energy, specific surface area, the influence of pore shapes and sizes, enthalpy, and the adsorption mechanisms of hydrogen molecules in approaches to increasing gravimetric and bulk hydrogen-storage capacity in nanoporous carbon materials. Many experimental studies have been devoted to the development of methods for the preparation of nanoporous carbon from various precursors and the investigation of their adsorption capacity for hydrogen. In [14], the ability of activated carbon to adsorb hydrogen obtained by carbonization of rice husk, depending on the conditions of chemical activation using KOH, was studied. The authors report that by varying the amount of KOH during activation, the specific surface area of activated carbon can be increased with micropore content in the range of 0.6–0.8 nm, the most optimal for hydrogen sorption. The maximum hydrogen sorption of 2.85 wt.% at 77 K was achieved by treating rice husk with KOH at a 1:1 ratio. Nitrogen-containing activated carbons with a specific surface area of $526-2386 \text{ m}^2/\text{g}$ and pore volume in the range of $0.26-1.16 \text{ cm}^3/\text{g}$ were synthesized [15]. The authors studied the effect of pore size and nitrogen content on hydrogen adsorption at 77 K and found that the adsorption capacity depended on the ultramicropore volume and pore size in the range of 0.5–0.7 nm, but is not related to the specific surface area, total pore volume, and nitrogen content. The authors of [16] synthesized three types of porous carbon materials from chitosan, having approximately the same specific surface area but with different pore size distributions, and studied the effect of pore size on the overall hydrogen-storage capacity. The authors found that nanopore sizes between 1.5 and 2.5 nm in porous carbon increased the hydrogenstorage capacity under high pressure, while the predominant content of micropores smaller than 1.5 nm was most effective for hydrogen storage, regardless of the pressure value. The authors also showed that mesopores larger than 2.5 nm are not involved in the process of increasing hydrogen-storage capacity. In [17], nanoporous carbon with different specific surface areas and pore size distribution was synthesized from corn cobs and their ability to absorb hydrogen was studied. The authors found that ultramicropores with sizes from 0.65 to 0.85 nm effectively absorb hydrogen at a temperature of 77 K and a pressure of 1 bar, and micropores with sizes from 0.85 to 2.00 nm are effective in absorbing hydrogen at higher pressures.

In [18], polymer-based nanoporous carbon with a specific surface area in the range of $1680-2320 \ \mu\text{m}^2/\text{g}$ and a specific pore volume in the range of $0.78-1.39 \ \text{cm}^3/\text{g}$ was obtained under different conditions of vapor activation. The authors investigated the ability of the obtained materials to adsorb hydrogen at a temperature of 298 K and a pressure of 10 MPa depending on the pore size distribution. It was found that the maximum efficiency of hydrogen adsorption was recorded at a temperature of 298 K and a pressure of 10 MPa, with micropore content mainly in the range of 0.63–0.78 nm. In [19], several nanoporous carbon samples with different pore size distributions were obtained by varying the preconditioning and chemical activation conditions of Ketjenblack (EC-600JD). The authors proposed a new calculation model based on density functional theory (DFT) to determine the contribution of pore size to the adsorption of gas molecules. In the proposed calcu-

lation model, a comparative evaluation of the contribution of the volume of micropores divided into groups <0.6, 0.6-1.0, and 1-2 nm on the adsorption capacity of the obtained materials on hydrogen at ambient pressure as a function of temperature was carried out. The studies showed that, at low temperatures, 77–87 K micropores smaller than 1 nm are 2–3 times more effective for hydrogen adsorption than micropores 1–2 nm in size, but it was noted that at high temperatures 273–298 K pore sizes do not have a significant effect on hydrogen adsorption. The authors of [20] conducted experimental and numerical studies to reveal the influence of the geometry and pore size on the adsorption characteristics of hydrogen molecules, activated carbon with disordered structure, and found that the main factor in increasing the adsorption efficiency of hydrogen molecules in porous materials is not the geometric shape of pores, but a narrow pore size distribution <1 nm. In [21], the authors proposed an effective way to increase the specific surface area of nanoporous carbon obtained from biomass by the partial decomposition of lignin and hemicellulose in an aqueous mixture of Na₂SO₃ and NaOH before the carbonization process. The obtained nanoporous carbon had a specific surface area of 2849 m^2g^{-1} , a total pore volume of $1.08 \text{ cm}^3 \text{g}^{-1}$, contained >92% micropores, adsorbed 3.01 wt.% of hydrogen at 77 K temperature and 1 bar pressure, and adsorbed 0.85 wt.% of hydrogen at 50 bar pressure at room temperature. The paper [22] reviews the current advances in the field of hydrogen storage on various carbon adsorbents and discusses and evaluates the concept of hydrogen storage in porous materials based on the spillover effect mechanism. To realize the spillover effect mechanism, the authors introduced metal nanoparticles (Pd, Pt, Ni) into the structure of porous material as catalysts for hydrogen dissociation. The dissociated hydrogen atoms migrate from the metal particles into the pores of the porous material with lower activation energy (<10 kJ/mol). An attractive feature of this concept is the possibility of operating hydrogen-storage systems at room temperature. More recent studies [23–25] have also shown that the addition of metal nanoparticles (Pd, Ni, and Pt) to carbon materials doped with heteroatoms (B, N) can improve hydrogen storage due to hydrogen dissociation followed by a spillover effect mechanism.

Thus, a review of studies on the use of nanoporous carbon for hydrogen storage underscores the importance of pore size optimization to improve the efficiency of hydrogen adsorption. Consequently, the development of methods for the synthesis of nanoporous carbon materials with a given pore size distribution in the optimized range is an urgent task. Plant raw materials have a multicomponent chemical composition and complex cell structure morphology. The intercellular substance consists of bundles of cellulose fibers surrounded by hemicellulose, which are bound in a composite by a polyphenolic lignin binder [26]. During the carbonization of plant raw materials, chemical transformations occur at the interface, the efficiencies of which are limited mainly by diffusion constraints. The accessibility of the inner surface can be increased by using activating influences that cause the loosening of the intercellular substance and its partial depolymerization. The main distinguishing feature and novelty of the proposed research is the use of preliminary mechanical activation of the initial rice husk before the carbonization process as a tool to control the process of porosity formation in nanoporous carbon material obtained in the process of subsequent carbonization. The possibility of controlling the process of pore formation is explained by the fact that by changing the conditions of mechanical activation it is possible to regulate the degree of destruction of the main components of plant raw materials, cell partitions, cellulose, and lignin, thus increasing the selectivity of the removal of volatile components in the process of carbonization to control the size and volume of the formed pores. This paper presents and discusses the results of studies on the optimization of conditions of mechano-activation, carbonization, and chemical activation to obtain nanoporous carbon with maximum micropore content and studies the hydrogen sorption characteristics.

2. Experimental Part

2.1. Synthesis of Rice Husk-Based Nanoporous Carbon and Its Decoration with Metal Nanoparticles

Rice husk, a natural and renewable waste product of plant origin, poses a significant environmental challenge when accumulated in large quantities. This is due to its slow decomposition rate and the substantial amount of organic compounds it contains [27]. On the other hand, during the thermal carbonization of rice husk from lignocellulosic fractions, micropores are formed, and the removal of silicon leads to the formation of mesopores, which, under the right choice of conditions, makes it possible to produce nanoporous carbon with optimal required characteristics. In the proposed work, rice husk with the basic chemical composition: $\sim 22\%$ lignin; $\sim 38\%$ cellulose; $\sim 20\%$ hemicellulose; and $\sim 20\%$ silicon dioxide (SiO₂) was used as a precursor to produce nanoporous carbon.

The production of nanoporous carbon was carried out in three stages: preliminary mechanical activation of the initial plant raw material, thermal carbonization, and chemical activation in an inert medium. Mechanical activation was carried out in a high-speed ball mill with 3D motion MSK-SFM-3. Before mechanical activation, rice husks were washed with distilled water to remove side contaminants and dried in a vacuum desiccator for 10 h at 120 °C. Traditionally, the degree of influence of mechanical activation on the structural changes in the studied material is regulated by varying the duration of milling time. During experimental studies, it was found that to regulate the process of porogenization in the resulting carbon, a more appropriate parameter to vary is the ratio of the mass of grinding balls to the volume (mass) of plant raw materials loaded. To prevent oxidation processes, the carbonization and thermochemical activation process was carried out in an argon environment. Potassium hydroxide (KOH) was used as a chemical activator to increase porosity. Figure 1 shows the scheme of nanoporous carbon production by the preliminary mechanical activation of rice husk followed by the processes of carbonization and chemical activation.



Figure 1. Scheme of mechanical activation (a) and activation process (b) of nanoporous materials.

The duration of the mechanical activation process of rice husk was 20 min with the ceramic grinding balls of 47 g mass. To determine the effect of mechanical activation on the porosity-formation process, the mass of processed rice husk was varied from 1 to 5 g. To present the results of the studies, the samples were labeled as NC-0 (original rice husk not subjected to mechanical activation), NC-1, NC-2, NC-3, NC-4, and NC-5, where the last digit corresponds to the mass of original rice husk loaded into the 3D mill. All samples were carbonized at 510 °C for 60 min under argon gas (flow rate ~0.005 L/min, heating rate 5 °C/min); then, the carbonization products were mixed with KOH powder at a mass ratio of 1:4, subjected to thorough mixing, and kept in a desiccator for 8 h at 360 °C to allow for impregnation with molten potassium hydroxide. Then, the obtained mixture was subjected

to a thermochemical activation process. The temperature in the reactor was increased at a rate of 5 °C/min until a temperature of 850 °C was reached, and at this temperature activation was carried out for 90 min in argon gas. After the activation process, the samples were thoroughly washed with 0.05 M HCl solution to remove KOH residues. To remove the residual HCl, the resulting activated carbon was washed with warm distilled water to neutral pH = 7 and then dried in a vacuum desiccator at 120 °C for 10 h, resulting in nanoporous carbon.

To explore the potential of increasing the hydrogen-adsorption capacity of the resulting nanoporous carbon due to the spillover effect mechanism arising from the introduction of hydrogen dissociation catalysts into the structure of nanoporous material [23–25], studies were carried out to develop methods for creating carbon-nickel (NC-2/Ni) and carbon–platinum (NC-2/Pt) composites. Carbon–metal composites were obtained by the impregnation of nanoporous carbon NC-2 with a solution of metal salts and subsequent reduction of metal nanoparticles from metal salts by thermochemical action. During the impregnation process, the salt solution penetrates the pores of the carbon material and, accordingly, the percentage of reduced metal nanoparticles will depend on the number of pores in which the salt solution settles. To change the percentage of metal nanoparticles in the composite material, the nanoporous material was impregnated with salt solutions by using two methods. In the first method, to obtain a composite material with a low metal nanoparticle content, impregnation was carried out by mixing a salt solution with nanoporous carbon at room temperature and atmospheric pressure. In the second method, impregnation was carried out in an autoclave at a temperature of 160 °C and an overpressure of $20-25 \text{ kgf/cm}^2$. Experimental studies have shown that high pressure allows for a significant increase in the filling of pores with salt solution and, consequently, an increase in the percentage of metal nanoparticles in the obtained composites. The percentage content of metal nanoparticles was evaluated by comparing the mass of the composite material with the mass of the initial nanoporous carbon NC-2 at the same bulk volume of 10 cm³. Aqueous 0.4 M nickel nitrate hexahydrate Ni(NO₃)₂-6H₂O solution was used to obtain the carbon–nickel composite. An ethanolic 0.1 M solution of platinum hydroxide H₂[PtCl₆]-6H₂O was used to make the carbon–platinum composite. To make the carbon– nickel and carbon-platinum composites, NC-2 nanoporous carbon was impregnated with aqueous Ni(NO₃)₂-6H₂O solution or ethanol solution of hydrogen hexachloroplatinate $H_2[PtCl_6]-6H_2O$. The nanoporous carbon impregnated with the salt solution was washed and dried at 100 °C for 6 h in an argon atmosphere. To form the nickel oxide nanoparticles, the dried material was heat treated for 60 min in an argon atmosphere in a CVD furnace at 300 °C. Subsequent recovery of the nickel nanoparticles from nickel oxide was carried out by starting the system with a mixture of argon and hydrogen at a ratio of 100:10 and a temperature of 500 °C for 60 min. To obtain a carbon–platinum composite, dried samples were heat treated at 275–300 °C with $H_2[PtCl_6]-6H_2O$ crystalline hydrate nanoparticles in an argon atmosphere for 60 min. During the heat treatment, H₂[PtCl₆]-6H₂O crystal hydrates decomposed to form platinum chloride. To recover platinum metal nanoparticles from platinum chloride, a 10% mixture of hydrogen and argon was launched and incubated at 300 $^{\circ}$ C for 60 min. The experimental studies show that it is possible to form metal particles on the carbon surface in the interstitial space between the carbon particles with sizes largely exceeding the nanoscale range. Preventing the formation of large particles on the carbon surface in the interstitial volume was achieved by the thorough washing of porous carbon impregnated with the solution of cold distilled water. Washing washes out up to 95% of the metal salt in the interstitial space between the carbon particles, which significantly reduces the formation of large metal nanoparticles in the composite material.

2.2. Material Characterization

The structural and morphological characteristics of the obtained samples of nanoporous carbon and carbon–metal composites were investigated using a Quanta 200i 3D scanning electron microscope. The specific surface area, pore size distribution, and micropore vol-

ume were investigated using an automatic micropore analyzer, Autosorb IQ. The specific surface area was calculated using the Brunauer–Emmett–Taylor (BET) method, the specific surface of micropores was determined using the Dubinin–Radushkevich method (D-R method), and the pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) method.

2.3. Methods of Measuring Adsorption Characteristics

Figure 2a shows the assumed mechanism of migration of hydrogen atoms dissociated on metal particles into the pores of porous material. Studies of the adsorption characteristics of the obtained nanoporous materials were carried out using an in-house developed Sievert apparatus, the scheme of which is presented in Figure 2b.



Figure 2. Illustration of possible pathways of hydrogen migration during hydrogen-storage spillover effect (**a**), scheme of the installation (**b**) to study the process of hydrogen sorption and desorption by nanoporous materials.

The pipeline and parts of the unit were made of special 12X18H10T grade stainless steel, designed for high-pressure operation in the temperature range from -196 to 600 °C. SS-42XS4 grade shut-off valves provided tightness, and when 10 bar hydrogen pressure was applied for 24 h, the pressure in the system decreased by 20%. The pressure in the system was recorded by using a high-precision sensor, brand OVEN PD100-DI, which determines the pressure with an accuracy of 0.001 kgf/cm² using a software application.

Before measurements, nanoporous carbon was degassed by pumping the system for 5 h while simultaneously heating the sample vessel with the adsorbent sample to a temperature of 500 °C. The nanoporous carbon was loaded into the sample vessel until it was filled; depending on the bulk density of the nanoporous carbon, its mass varied between 1560 and 1580 mg. The adsorption temperature was monitored using liquid nitrogen. The amount of adsorbed hydrogen in the nanoporous carbon samples was calculated from the data of the pressure-temperature dependence of the pressure change at constant volume. At a temperature of 20 °C, hydrogen was introduced into the system with adsorbent at a fixed pressure of 9 kgf/cm^2 , after which the hydrogen access valve was closed and a graph of the pressure-temperature dependence of the pressure change at constant volume was plotted. To calculate the amount of adsorbed hydrogen, the actions described above were repeated, but instead of nanoporous carbon in the vessel for the image carbon black (CB) was loaded, which does not adsorb hydrogen. In the experiments with nanoporous carbon, the value of the steady-state pressure is the sum of the pressure arising from the compression of hydrogen at lowering the temperature in the vessel with the sample, and the pressure arising from the adsorption of hydrogen. In experiments with carbon black, the process of adsorption of hydrogen is absent, and the value of the steady-state pressure arises due to the compression of hydrogen at lowering temperatures in the vessel with the sample. Thus, the pressure difference between the obtained data will be equivalent to the amount of hydrogen adsorbed by nanoporous carbon. The proposed method allowed us to calculate the amount of adsorbed hydrogen in the investigated sample at any given temperature. The actual working volume of the unit, considering the volume occupied by nanoporous or black carbon, calculated using helium showed that they differed by hundredths of a fraction and that the difference can be neglected. The volume of the vessel for loading the sample under study was $\approx 10 \text{ cm}^3$, and the total volume of the unit considering the loaded nanoporous carbon was $\approx 229 \text{ cm}^3$. In the experiments, helium and hydrogen of special purity grade "7.0" 99.99999 were used.

3. Results

3.1. Texture Characteristics of Nanoporous Carbon

Plant raw materials have a multicomponent chemical composition and a complex morphological cellular structure. The intercellular substance consists of bundles of cellulose fibers surrounded by hemicellulose, which are bound in a composite by a polyphenolic lignin binder. During the carbonization of plant raw materials, chemical transformations take place at the interface, the efficiencies of which are mainly limited by diffusion constraints. The accessibility of the inner surface can be increased by using activating effects that cause the loosening of the intercellular substance and its partial depolymerization. Preliminary mechanical activation of the initial rice husk provides access to its internal structure and increases the efficiency of carbonization processes.

The porosity characteristics of the obtained samples were investigated by adsorption– desorption analysis using nitrogen N₂ at 77 K. Figure 3 presents adsorption–desorption isotherms (Figure 3a) and a graph showing the value of total pore volume as a function of pore size distribution (Figure 3b) for the nanoporous carbon samples obtained under different mechanical activation conditions.



Figure 3. Adsorption–desorption isotherms (**a**) and total pore volume as a function of pore size distribution (**b**) for samples obtained under different mechano-activation conditions.

The analysis shows that the nitrogen adsorption–desorption isotherms of samples NC-0, NC-1 NC-2, and NC-5 belong to type I according to the IUPAC classification [28]. The graph shows that these samples show a sharp increase in adsorption in the region of low relative pressures, and after reaching a certain pressure the adsorption process stabilizes and the adsorption growth curve shows a well-defined plateau, indicating the microporous structure of the studied samples. Samples NC-3 and NC-4 show, to a greater extent, a

typical adsorption curve belonging to type IV and indicate an increase in the volume of mesopores in the studied samples [28]. Hysteresis was observed in all the samples, indicating the presence of mesopores, but the shapes of the isotherm curves indicate that samples NC-0, NC-1, NC-2, and NC-5 contain fewer mesopores compared to samples NC-3 and NC-4. Further studies of pore size distribution and the calculation of micropore volumes by the D-R method confirm this regularity. Table 1 shows the textural parameters of the obtained porous carbon samples, specific surface area according to BET, specific surface area of micropores by the D-R method, as well as the volume and average pore width calculated by the BJH method.

Sample Designation	S _{BET} , m²/g	S _{BET} , m ² /g D-R Method	V _{BJH} , cm ³ /g	R _{BJH} Å
NC-0	2386	2754	0.251	19.251
NC-1	2735	2649	0.706	17.136
NC-2	2713	3099	1.625	17.198
NC-3	2353	2133	1.715	19.259
NC-4	2482	2863	2.215	19.263
NC-5	2007	2436	0.525	19.201

Table 1. Texture parameters of the obtained porous carbon samples.

Sample NC-1 has the highest specific surface area, but in sample NC-1, the total pore volume and specific surface area of micropores calculated by using the D-R method are smaller than in sample NC-2. It will be shown below that the increase in specific surface area in sample NC-1 is not due to porosity but to dispersion.

Figure 4 presents the SEM images, which can be used to evaluate the degree of influence of the mechanical activation conditions on the microstructure of the obtained nanoporous carbon. We attribute the change in the porosity characteristics of the obtained carbon materials to the influence of the mechanical activation conditions on the initial rice husk. The mass of grinding balls and the duration of processing time in the 3D mill were constant, and the degree of influence of mechanical activation on the destruction of the rice husk structure was controlled by changing the amount of sample loaded. Samples NC-0, NC-3, NC-4, and NC-5 have a relatively similar average pore size in the range of 1.91–1.92 nm but differ in the specific surface areas calculated by using the BET method, specific surface areas of micropores calculated by using the D-R method, and total pore volumes calculated by employing the BJH method. In sample NC-5, although mechanical activation did not significantly pulverize the grains and destroy their microstructure (Figure 4b), an increase in total pore volume was observed. We attribute the increase in the total pore volume to the intensification of the pore-formation process in the volume of grains due to partial destruction of their surface.

In samples NC-3 and NC-4 (Figure 4c,d), the impact of mechanical activation led to more intensive destructions of the grain microstructure with the formation of numerous defects on their surfaces, contributing to the formation of mesopores. In parallel, due to the increased accessibility of the internal structure of grains, the process of micropore formation was intensified. Mechanical activation of the NC-2 sample led to the complete destruction of rice husk grains into small particles, but each particle retained the original grain microstructure (Figure 4e). Grinding of rice husk significantly increased the total surface area and opened access to the internal microstructure of the grains, and this circumstance during further carbonization and thermochemical activation process promotes the intensive formation of micropores with an average pore width of 1.71 nm. In sample NC-1, micropores with a pore width of 1.71 nm were also formed, but compared to sample NC-2, the total volume of micropores decreased and the BET specific surface area increased. When the mass of loaded rice husk was reduced to 1 g by increasing the intensity of grain grinding, the number of small fragments with destroyed microstructure in which the formation of pores was impossible increased (Figure 4e), and the total volume of pores



decreased. The increase in the BET method specific surface area was due to the increase in dispersibility [29].

Figure 4. SEM images of nanoporous carbon obtained under different conditions of mechanical activation of initial rice husk: (a)—NC-0; (b)—NC-5; (c)—NC-4; (d)—NC-3; (e)—NC-2, (f)—NC-1.

The results show that the nanoporous carbon obtained from mechanically activated treated rice husk compared to untreated rice husk exhibited an increase in the BET method specific surface area from 2386 to 2713 m²/g, specific surface area of micropores calculated by using the D-R method from 2754 to 3099 m²/g, and total pore volume calculated by using the BJH method from 0.251 to 1.625 cm³/g. Thus, the newly proposed approach to control the pore-formation process in nanoporous carbon obtained from plant raw materials allows for the adaptation of adsorption characteristics for hydrogen storage.

One of the promising methods for increasing the adsorption capacity of hydrogen adsorbents is the use of the spillover effect mechanism. To improve the adsorption characteristics of carbon porous materials using the spillover effect, metal nanoparticles (Pd, Pt, Ni) capable of dissociating a hydrogen molecule into atoms are introduced into their structure. The dissociated hydrogen atoms migrate from the metal particles into the pores of the porous material, which have a low activation energy (<10 kJ/mol). An attractive feature of the spillover effect is the possibility of creating hydrogen-storage systems that function at room temperature, and research in this area is of relevance. To study the possibilities of increasing the adsorption capacity due to the spillover effect, carbon–nickel (NC-2/Ni) and carbon–platinum (NC-2/Pt) composites were created based on nanoporous carbon NC-2 using the method described in paragraph 2.1 of this article. The obtained composite samples were investigated by using SEM, TEM (transmission electron microscopy), and XRD analyses to determine the compositions and structural characteristics. Figure 5 shows SEM and TEM images of the created composites.



Figure 5. SEM images of the obtained composites: (a) NC-2/Ni_{10%} obtained without nickel salt washing; (b) NC-2/Pt10% obtained after nickel salt washing; (c) nickel nanoparticles located in mesopores; (d) platinum nanoparticles located in mesopores.

The analysis of the SEM images shows that in composites obtained without washing of the impregnated metal salt, many nickel particles with sizes more than 100 μ m were formed on the carbon surface in the interstitial space between carbon particles (Figure 5a). After washing the impregnated salt, the total content of nickel particles decreased with a simultaneous decrease in their size to 500–600 nm. Figure 5b–d shows the images of nickel and platinum nanoparticles located in the mesopores of nanoporous carbon formed after washing the impregnated salt. In the fragment of the TEM image, platinum nanoparticles located in the mesopores can be observed.

The X-ray diffraction analyses presented in Figure 6a,c reveal features of both pure nanoporous carbon and those decorated with nickel and platinum nanoparticles. It is of great significance that the doping process did not alter the graphitized structure, thus emphasizing the high content of organized carbon in these samples. The results of X-ray fluorescence spectroscopy also confirm the presence of nickel and platinum on the surface of the studied samples.



Figure 6. Raman spectroscopy (a) and XRD analysis (b,c) of the obtained samples.

Figure 6b illustrates the structural details of the nanoporous coal investigated by using Raman spectroscopy. The analysis shows the high intensity of the G and D peaks, indicating a progressed degree of graphitization in the sample. This, in turn, suggests improved electrical conductivity, making the material suitable for applications where ordered carbon structures are required. In addition, a weak 2D peak is observed, which usually indicates the presence of multiple layers of graphene in the structure [30]. Despite its small amplitude, this peak plays a key role in determining the structural ordering and electronic properties of the material.

3.2. Hydrogen-Adsorption Characteristics

The hydrogen-adsorption capacities of the obtained samples of nanoporous carbon, obtained under different conditions of preliminary mechano-activation of the initial rice husk at an adsorption temperature ≈ -190 °C, were determined by using the method described in Section 2.3. Figure 6a shows the graph of pressure change in the system as a function of temperature decrease in the sample vessel in the range from 20 to ≈ -190 °C. To determine the amount of adsorbed hydrogen by comparison, the graph shows the curves of pressure change as a function of temperature, built on the data obtained with carbon black and nanoporous carbon samples.

The analysis of the obtained results indicates that in the samples of nanoporous carbon, the amount of adsorbed hydrogen increases as the temperature decreases. This increase correlates with a decrease in average pore width and an increase in micropore volume. However, it does not depend on the total pore volume and the specific surface area, as calculated by using the BET method. These findings are consistent with the data presented in [20]. The maximum hydrogen capacity of 3.7 wt.% was observed in sample NC-2, in which the average pore width was 1.71 nm and the micropore volume calculated by using the D-R method was 3009 m²/g.

Table 2 summarizes the results of calculating the quantitative content of adsorbed hydrogen in the investigated nanoporous carbon samples.

The kinetics of the hydrogen-adsorption process by the NC-2/Ni and NC-2/Pt composites, in the temperature range from 20 to \approx –190 °C at pressures of 9 kgf/cm² and in different percentages of metal nanoparticles, were investigated (Figure 7).

In the experiments with NC-2/Ni_{20%}, NC-2/Ni_{10%}, and NC-2/Pt_{20%} composites, the final pressure in the system was higher compared to the pressure obtained in the experiments with nanoporous carbon NC-2. The results indicate that less hydrogen was adsorbed when the temperature in the adsorbent vessel was lowered to \approx -190 °C. In the NC-2/Pt_{10%}

composite material, the adsorption efficiency compared to NC-2 nanoporous carbon unmodified with metal nanoparticles increased by 7.8%. The obtained results indicate that the decoration of nanoporous carbon NC-2 with metal nanoparticles does not lead to a significant improvement in adsorption capacity at a temperature \approx -190 °C, i.e., no obvious influence of the spillover effect was observed.

Table 2. Results of calculation of the quantitative content of adsorbed hydrogen in the obtained samples of nanoporous carbon at a temperature of -190 °C.

Nanoporous Carbon Sample	NC-0	NC-1	NC-2	NC-3	NC-4	NC-5
Amount of adsorbed hydrogen in mass.% at \approx -190 °C	2.31	3.22	3.71	2.93	2.81	2.52
Pressure difference, kgf/cm ²	1.921	2.653	3.14	2.442	2.325	2.133
Mass of adsorbed hydrogen, g	0.035	0.048	0.055	0.044	0.042	0.037



Figure 7. Dependence of pressure–temperature variation in hydrogen adsorption for nanoporous coals (**a**) and NC-2/Ni and NC-2/Pt composites (**b**).

To determine the influence of the spillover effect on the adsorption characteristics of the NC-2/Ni $_{10\%}$ and NC-2/Pt $_{10\%}$ composites, measurements were carried out at room temperature using the following procedure. In the room where the measurements were carried out, the temperature was maintained between 19 and 21 °C using an air conditioner. Before the measurements, the system was degassed by pumping for 4 h while heating the composite sample vessel to 500 °C. Then, we waited until all parts of the system cooled down to ambient temperature in vivo. When the temperature reached 20 °C, the valve separating the sample vessel from the pipeline was closed, hydrogen was launched into the pipeline, and the pressure value was recorded to the nearest 0.001 kgf/cm². After these actions, the valve separating the sample vessel from the pipeline system was opened and the value of the steady-state equilibrium pressure was recorded. All the above steps were repeated with pure NC-2 nanoporous carbon. The pressure difference occurring in the experiments with composites and NC-2 nanoporous carbon was used to evaluate an increase or decrease in the hydrogen-adsorption efficiency of the composites. Table 3 summarizes the results of the hydrogen-adsorption studies of NC-2 nanoporous carbon and the NC-2/Ni_{10%} and NC-2/Pt_{10%} composites at 20 $^{\circ}$ C and 9 kgf/cm² pressure.

Type of Material	Initial Pressure in the System, kgf/cm ²	Pressure in the System after Combining the Sample Vessel with the Pipeline, kgf/cm ²	Mass of Adsorbed Hydrogen, g	Amount of Adsorbed Hydrogen, wt.%
NC-2	9.009	8.341	0.0121	0.81
NC-2/Ni _{10%}	8.996	8.320	0.0124	0.83
NC-2/Pt _{10%}	9.005	8.094	0.0167	1.11

Table 3. Results of studies on hydrogen adsorption by nanoporous carbon NC-2 and composites NC-2/Ni_{10%} and "carbon–platinum" NC-2/Pt_{10%} at 20 °C temperature and 9 kgf/cm² pressure.

The conducted studies show that compared with nanoporous carbon NC-2 at a 20 °C temperature and 9 kgf/cm² pressure, there is an increase of 2.4% in hydrogen adsorption in the composite NC-2/Ni_{10%}, and in the "carbon–platinum" NC-2/Pt_{10%} composite, there is an increase of 27% in sorption capacity, which is explained by the occurrence of the spillover effect.

4. Conclusions

The main feature and novelty of the conducted research is the use of preliminary mechanical activation of the initial rice husk as a tool for controlling the process of porosity formation in nanoporous carbon material during its production by carbonization and thermochemical activation methods. The obtained results showed that in nanoporous carbon obtained by preliminary mechanical activation of the initial rice husk, compared to untreated rice husk, it was possible to achieve a maximum increase from 2386 to 2713 m^2/g in the specific surface area calculated by using the BET method, from 2754 to 3099 m^2/g in the specific surface area of micropores calculated by adopting the D-R method, and from 0.251 to $1.625 \text{ cm}^3/\text{g}$ in total pore volume calculated by employing the BJH method. Preliminary mechanical activation of the initial rice husk before the carbonization process improved the microporosity of the obtained nanoporous carbon and increased its adsorption capacity for hydrogen at \approx -190 °C temperature and 9 kgf/cm² pressure by 29.7% compared to nanoporous carbon obtained based on rice husk that was not subjected to mechanical activation. Thus, a new approach has been proposed for controlling the process of pore formation in nanoporous carbon obtained from plant raw materials, allowing for optimization of its adsorption characteristics at hydrogen storage. The carbon-platinum composite NC-2/Pt_{10%} was created at 20 °C temperature and 9 kgf/cm² pressure, and it showed a 27% increase in sorption capacity compared to pure nanoporous carbon NC-2, which is explained by the occurrence of the spillover effect.

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