



Article Carbon-Supported Nickel Catalysts—Comparison in Alpha-Pinene Oxidation Activity

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Abstract: In this work, carbon-supported nickel catalysts with different Ni content (1, 2.5, 5, 10, and 20 wt%) were tested in the oxidation of alpha-pinene in solvent-free reaction conditions. The process of catalyst preparation consisted of two stages. In the first stage, the activated carbon from spent coffee grounds was obtained. In the second stage, the active phase in the form of nickel compounds was applied using two methods: (1) the impregnation of the material with the nickel salt solution, and next reduction in H₂, and (2) the hydrothermal method in the autoclave using the reductor and the reaction stabilizer. The obtained catalysts were subjected to the following instrumental studies: FT-IR, XRD, SEM, and N₂ adsorption at -196 °C. The performed catalytic tests showed that the catalysts containing 5 wt% of Ni (porous material obtained by the impregnation method) and 1 wt% of Ni (porous material obtained by the hydrothermal method) were the most active in the oxidation of alpha-pinene, and the main oxidation products were alpha-pinene oxide, verbenol, and verbenone. Ultimately, the hydrothermal method of catalyst preparation turned out to be more advantageous because it allows one to obtain higher selectivities of the epoxide compound, probably due to the greater stability of this organic compound in pores.

Keywords: carbon-supported catalysts; activated carbon; nickel compounds; oxidation of alpha-pinene; alpha-pinene oxide; verbenone; verbenol

1. Introduction

Due to their developed specific surface and the presence of macropores, mesopores, and micropores, as well as the presence of different functional groups on the surface, activated carbons are gaining more popularity as functional materials for various applications [1]. Activated carbons can be obtained from alternative precursors of natural origin and commercial carbon solid precursors [2,3]. The first group includes waste products from the agriculture and food industries [4], and also lignocellulosic materials [5]. Most agricultural waste biomasses contain chemical ingredients that have a high carbon content, which makes them suitable precursors for activated carbon production [6]. In addition, activated carbons produced from agricultural waste have a large specific surface area and are characterized by a well-built internal pore structure [7]. Moreover, the advantage of producing carbonaceous materials from biomass is the fact that this raw material is cheap and easily available [2]. The second group consists of materials used commercially on a large scale [8]. Carbon precursors used in the production of activated carbons on the industrial scale are wood, anthracite, lignite, coal, and peat, but these materials are limited in terms of quantity and are non-renewable [2]. Global coffee production is around 7 million tons of beans per year. Spent coffee grounds are produced as waste products in the production of instant coffee and the brewing of coffee. It was estimated that 1000 kg of green coffee produces 650 kg of coffee grounds [9]. Vegetable tannins, chlorogenic acid,



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Copyright: © 2023 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/). and caffeine are the chemical compounds present in spent coffee grounds that can pose a risk to the environment if they are not properly disposed of and neutralized, making it difficult to reuse them into value-added products [10]. The presence of these compounds limits the possibility of using this biomass as an additive to animal feed [11]. It has been proven that caffeine and tannins have an adverse effect on the aquatic environment [12]. In turn caffeine also has an adverse effect on the growth of plants [13], fungi [14], and bacteria [15]. Moreover, chlorogenic acid has an adverse effect on seed germination and plant growth, which limits the use of this waste as an additive to plant fertilizers [16]. Currently, used coffee grounds are processed into biofuels [17], applied as a component of organic compost [18], used as raw material for obtaining bioethanol [19], and used as a precursor for activated carbons production [20].

Carbon materials are used in an increasing number of applications in catalysis, either as supports for the active phases or as catalysts on their own. Usually, metal nanopoarticles are the active phase of the catalyst. Bottom-up methods are used to obtain metal nanoparticles with high stability and high chemical purity, as well as of desired sizes [21]. These methods include hydrothermal synthesis, co-precipitation of nanoproducts in solution, sonication [22], and chemical reduction, including hydrogen jet reduction [23]. Bottom-up methods use metal oxides and salts as precursors for metal nanoparticles and substances that reduce the precursors to specific metallic structures. In these techniques, the dispersion mode, shape, and dimensions of the nanoparticles can be controlled by the modification of the reaction conditions [24]. Only a few publications refer to the synthesis of carbonaceous catalysts containing Ni in a structure that has been described in the literature. Lestinsky et al. [25] synthesized carbonaceous-nickel catalytic materials using microwave pyrolysis. Fildago et al. [26] deposited metallic nickel on the commercial activated carbon. To obtain metallic nickel from nickel compounds, the team applied a hydrogen reduction method. In turn, Malobela [27] synthesized a bimetallic Cu-Co catalyst based on activated carbon. The metallic nanostructures were obtained thanks to the reduction of the metal precursor in the hydrazine solution. To produce nickel-containing carbon catalysts, the method of thermal decomposition of the metal precursor in a tube furnace in the presence of N_2 [28] and a co-impregnation method followed by calcination [29] were also used. In recent decades, metallic nanoparticles have also attracted attention as highly active and ecological catalysts in many processes [30], including oxidation reactions of many compounds. According to available knowledge, only a few studies concern the use of metal catalysts for the oxidation of alpha-pinene. The oxidation of alpha-pinene is most often catalyzed by nanoparticles of copper [31], cobalt [32], iron [33], ruthenium [34], titanium [20], vanadium [35], and bimetallic nanoparticles of Au-Cu [36]. Alpha-pinene belongs to a broad group of compounds which are called terpenes. This organic compound is the main secondary metabolite of many plants, and it occurs in large amounts in turpentine conifers [37]. From an economic point of view, the richness of terpenes in nature and the possibility of obtaining them from natural sources (biomass) make them a promising starting material for the synthesis of many valuable compounds [38]. The main products of alpha-pinene oxidation are alpha-pinene oxide, verbenol, and verbenone [34]. These compounds are widely used in the perfume and cosmetic industries and in the production of aromas [39]. In addition, verbenone is used for synthesis of taxol, a therapeutic agent for the treatment of cancer [40].

The aim of our work was to find an effective and inexpensive method of transformation of waste from the food industry (spent coffee grounds) into active carbon-supported nickel catalysts as an added value. First, a high-temperature carbonization process and chemical activation with KOH were used to convert this waste into valuable carbon material. The obtained activated carbon was used as the support for the active phase (nickel nanoparticles) of the catalysts. Next, the influence of the textural parameters of the carbon catalyst, the method of applying the active phase (method of impregnation of the carbon material with the nickel salt solution and the reduction in H_2 , and the hydrothermal method synthesis in the autoclave) and content of Ni on the catalytic activity of the obtained catalysts in the oxidation of alpha-pinene was investigated. According to the available knowledge, the use of such catalysts for the oxidation of alpha-pinene has not been described in the literature. In this study, two of the most widely used methods for the preparation of heterogeneous catalysts were used: the impregnation method and the hydrothermal method. The advantages of these methods are the simplicity of execution, the minimal amount of waste, and the low cost [41]. Compared to other metals commonly used as catalysts for oxidation reactions, nickel salts are inexpensive precursors. The literature data indicate that the price of NiCl₂ is USD 0.1 per 1 mmol, while $PtCl_2$ —USD 32.2/1 mmol, AuCl₃—USD 35.6/1 mmol, and RhCl₃—USD 51.8/1 mmol [42]. The catalysts described in the literature and mentioned in the introduction required the reaction to be carried out in the presence of a solvent (usually chloroform, acetonitrile) and/or an oxidant other than oxygen (including H_2O_2 or tert-butyl hydroperoxide (TBHP)). It is important to note that the use of catalysts obtained by our team allows the oxidation of alpha-pinene to be carried out without solvents, making this method of carrying out the process environmentally friendly and cost effective (due to the absence of high costs of recovery and disposal of solvents).

2. Materials and Methods

2.1. Preparation of Activated Carbon (AC)

The synthesis of the activated carbon from biomass was carried out according to the methodology previously developed and described by our research team [20]. In this method, spent coffee grounds were washed several times with deionized water and dried. Next, this biomass was mixed with the chemical activator—an aqueous saturated KOH solution (Sigma-Aldrich, Burlington, MA, USA) and carbonized in the furnace (Alpina, Konin, Poland) at 800 °C for 1 h and under nitrogen atmosphere (99.999%, Messer, Chorzów, Poland). After carbonization, the sample was prewashed with distilled water, then flooded with 1 M water solution of HCl (37%, Sigma-Aldrich, Burlington, MA, USA), and washed again with distilled water to remove inorganic residues.

2.2. Preparation of Metallic Catalysts

2.2.1. Impregnation of Activated Carbon with Nickel Salt Solution and Reduction with Hydrogen

Into each of five flasks, 1 g of the activated carbon from coffee grounds was placed. Specific amounts of NiCl₂ · $6H_2O$ (97%, POL-AURA, Dywity, Poland) in 150 mL of distilled water were weighed into each flask so that there was (in wt%): 1%, 2.5%, 5%, 10%, and 20% nickel in 1 g of the carrier, respectively. Next, to break down salt crystals into smaller structures, the flasks were placed (30 °C, 30 min) in an ultrasonic cleaner (CHEMLAND, Stargard, Poland). Next, the mixture of metal salt and activated carbon was placed in a vacuum evaporator (Heidolph, Schwabach, Germany). The process was carried out at 75 °C, with 70 rpm, until the solvent was completely evaporated. The obtained materials were then dried in the oven at 100 °C (POL-EKO, Wodzisław Śląski, Poland). The materials prepared in this way were placed in the self-assembled tube furnace with the temperature controller at the hydrogen (99.99%, Messer, Chorzów, Poland) flow rate of 2 L/h and at 300 °C (the temperature build-up rate was 10 °C/min). The sample was kept at the set temperature for 2 h, then the furnace was cooled to the ambient temperature. The obtained samples were labeled as follows: SCG_1%Ni_H₂; SCG_2.5%Ni_H₂; SCG_5%Ni_H₂; SCG_10%Ni_H₂; SCG_20%Ni_H₂.

2.2.2. Hydrothermal Method of Preparation of the Catalysts in the Autoclave

Into each of five flasks, 1 g of the activated carbon from coffee grounds was placed, and 150 mL of distilled water was added. Then, specific amounts of NiCl₂ \cdot 6H₂O (97%, POL-AURA, Dywity, Poland) in 150 mL were weighed into each flask, so that there was (in wt%): 1%, 2.5%, 5%, 10%, and 20% nickel in 1 g of the support, respectively. To facilitate the dissolution of the nickel salt in water, the mixtures were placed (30 °C,

30 min) in the ultrasonic cleaner (CHEMLAND, Stargard, Poland). Next, 10 mL of 0.5 M solution of CTAB (cetyltrimethylammonium bromide— $C_{19}H_{42}BrN$ (stabilizer)) (100%, Sigma-Aldrich, Burlington, MA, USA) in water was slowly added into each flask and everything was stirred for 15 min on the magnetic stirrer with 750 rpm, at the ambient temperature (CHEMLAND, Stargard, Poland). Then an appropriate amount of ascorbic acid (reductant) (99%, Sigma-Aldrich, Burlington, MA, USA) was added to each flask so that the molar ratio of reductant to nickel salt used was 1:1. Next the solutions were placed in the autoclave (Berghof, Eningen unter Achalm, Germany). The process was carried out at 180 °C and for 19 h. The materials were then washed several times with methanol (99%, POL-AURA, Dywity, Poland) and distilled water. The obtained materials were dried in the oven (POL-EKO, Wodzisław Śląski, Poland) at 100 °C. The obtained samples were labeled as follows: SCG_1%Ni_autoclave; SCG_2.5%Ni_autoclave; SCG_5%Ni_autoclave; SCG_10%Ni_autoclave; SCG_20%Ni_autoclave.

2.3. Characteristics of the Catalysts Obtained from Biomass

Characterization of the obtained carbon-supported nickel catalysts was performed based on the following instrumental methods: N₂ sorption measurements at -196 °C, XRF, XRD, FT-IR, and SEM. For the obtained catalytic materials, the total number of acid sites was also determined using the titration method.

To characterize the textural parameters of the materials with N₂ adsorption/desorption at $-196 \,^{\circ}$ C, a Quadrasorb evoTM Gas Sorption analyzer (Anton Paar, St. Albans, UK) was used. Before the studies, samples were degassed at 200 $\,^{\circ}$ C for 19 h. The specific surface area was estimated from the nitrogen adsorption data after the application of the Brunauer–Emmett–Teller (S_{BET}) equation. The total pore volume (V_{tot}) was calculated by the volume of N₂ adsorbed at a relative pressure of ~0.99. The DFT method (the density functional theory) based on nitrogen adsorption was used to calculate the volume of micropores and to determine the pore size distribution.

The elemental composition of the catalysts was analyzed by X-ray fluorescence spectroscopy. The studies were carried out with the use of the XRF Analyzer Model Nap8200MB (Guangdong, China).

The acid-sites concentrations were determined by the application of the acid-base titration method described by our research team [20]. Accordingly, 0.02 g of catalyst sample and 10 cm³ of 0.01 M water solution of NaOH (98%, Sigma-Aldrich, Burlington, MA, USA) were added to the flask. Next, the flask was shaken for 6 h at the ambient temperature. After this time, the material was filtered off. The pH of the filtrate was determined using titration with 0.01 M water solution of HCl (37%, Sigma-Aldrich, Burlington, MA, USA) in the presence of 1% phenolphthalein (POL-AURA, Dywity, Poland) as an indicator.

XRD analyses were performed to determine the structure of the obtained materials. The X-ray diffraction (XRD) patterns of the catalysts were recorded by an X-ray diffractometer (X'Pert–PRO, Panalytical, Almelo, The Netherlands, 2012), using Cu K (λ = 0.154 nm) as the radiation source, in the 2 θ range of 10–100° and with a step size of 0.026. The obtained diffractograms were analyzed by comparison of the position and intensity of the reflections on the obtained diffractograms with the standard diffractograms from the ICDD PDF4+2015 database based on the X'Pert HighScore computer program.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet[™] iS50 FTIR Spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA, 2021). The samples of materials for studies were prepared using the KBr pressed-disk technique. A KBr disk sample was prepared with 200 mg of dried KBr powder (99%, Sigma-Aldrich, Burlington, MA, USA) and 2 mg of catalyst sample. A pure KBr tablet was used as a blank for background subtraction. Sixty-four scans were averaged for each sample in the operating range of wavenumber 4000–400 cm⁻¹.

To visualize the surface structures of the obtained catalysts, the SEM pictures were taken with a scanning electron microscope (Neon40 Crossbeam, Carl Zeiss SMT GmbH, Oberchoken, Germany, 2009).

2.4. Alpha-Pinene Oxidation Method

The oxidation of alpha-pinene was carried out in a 25 cm³ glass reactor placed in an oil bath with an air bubble and a reflux condenser (CHEMLAND, Stargard, Poland). The stirring rate was 500 rpm. Molecular oxygen with a purity of 99.99% was used as the oxidant. The oxygen flow rate was 40 mL/min. For oxidation studies, 10 g of alpha-pinene (98%, Sigma-Aldrich, Burlington, MA, USA) was used. The oxidation was carried out at the temperature range of 90–110 °C, the catalyst content was changed in the range of 0.1–5 wt%, and the reaction time was tested from 10 to 300 min. After the reaction was completed, the post-reaction solution was separated from the catalyst using a centrifuge.

The procedure for performing the qualitative and quantitative analyses of the postreaction solutions using the GC method was presented in our previous work [43].

3. Results and Discussion

3.1. Characterization of the Obtained Ni-Modified Carbonaceous Materials

Nitrogen adsorption data were used to evaluate the specific surface area and porosity of the studied carbonaceous catalysts. Table 1 shows the textural properties of the Nimodified carbonaceous catalysts obtained from biomass (the used biomass was spent coffee grounds).

Sample	S _{BET} [m ² /g]	Vtot [cm ³ /g]	Vmic [cm ³ /g]
SCG_1%Ni_H ₂	1534	0.752	0.563
SCG_2.5%Ni_H ₂	1104	0.569	0.410
SCG_5%Ni_H ₂	926	0.483	0.405
SCG_10%Ni_H ₂	838	0.436	0.360
SCG_20%Ni_H2	569	0.305	0.246
SCG_1%Ni_autoclave	105	0.091	0.074
SCG_2.5%Ni_autoclave	46	0.081	0.051
SCG_5%Ni_autoclave	35	0.054	0.038
SCG_10%Ni_autoclave	22	0.040	0.012
SCG_20%Ni_autoclave	13	0.023	0.011

Table 1. Textural properties of the obtained Ni-modified carbonaceous catalysts.

It is observable that catalysts obtained from the spent coffee grounds by the impregnation and H₂ reduction method have surface area values in the range of 569–1534 m²/g, total pore volume values of 0.305–0.752 cm³/g, pore volume of micropores of 0.246–0.563 cm³/g, and pore volume of mesopores 0.059–0.189 cm³/g. For catalysts obtained by the hydrothermal method, the values of the above-mentioned textural parameters are as follows: 13–105 m²/g, 0.023–0.091 cm³/g, 0.0011–0.074 cm³/g, and 0.03–0.008 cm³/g, respectively. Sample SCG_1%Ni_H2 has the maximum specific surface area and total pore volume, and these values amount to 1534 m²/g and 0.752 cm³/g, respectively. In addition, this sample also has a maximum pore volume of mesopores (0.189 cm³/g). For the SCG_1%Ni_autoclave sample, the maximum specific surface area is 105 m²/g, the maximum pore volume is 0.091 cm³/g, and the pore volume of mesopores amounts to 0.017 cm³/g. The maximum pore volume of mesopores is visible for the SCG_2.5% Ni_autoclave sample. For all samples, the specific surface area and the pore volume decreased as the metal content increased. The XRF analyses showed the presence of the main elements in the studied catalysts (Table 2).

Insignificant Si contents (0.29–0.88 wt%) were recorded for all samples. In addition, the presence of Cl (0.44–1.00 wt%) and K (0.19–0.75 wt%) was noted for the catalysts prepared by the impregnation method. Amounts of Ni close to the values assumed in the methodology were recorded for all catalysts. A similar relationship was observed by Dongil et al. [44]. Figure 1 shows the adsorption isotherms measured on the catalysts prepared by the impregnation and reduction in the H₂ method (Figure 1a) and the hydrothermal method in the autoclave (Figure 1b).

Sample ——	(wt%)				
	Si	Cl	К	Ni	
SCG_1%Ni_H ₂	0.42	0.44	0.75	0.92	
SCG_2.5%Ni_H ₂	0.88	0.51	0.23	2.50	
SCG_5%Ni_H ₂	0.62	0.91	0.34	4.91	
SCG_10%Ni_H ₂	0.52	0.97	0.19	9.90	
SCG_20%Ni_H ₂	0.29	1.00	0.16	19.99	
SCG_1%Ni_autoclave	0.88	-	-	1.05	
SCG_2.5%Ni_autoclave	0.53	-	-	2.57	
SCG_5%Ni_autoclave	0.57	-	-	5.08	
SCG_10%Ni_autoclave	0.93	-	-	10.31	
SCG_20%Ni_autoclave	0.39	-	-	19.99	

Table 2. Results obtained by the XRF method for Ni-modified carbonaceous catalysts.



Figure 1. Adsorption isotherms for catalysts obtained by: (a) the impregnation and reduction in H_2 method, and (b) the hydrothermal method in the autoclave.

The adsorption isotherms for SCG_5%Ni_H₂, SCG_10%Ni_H₂, and SCG_20%Ni_H₂ materials are classified according to the IUPAC classification as a type Ia. It should be noted that isotherms of SCG_1%Ni_H₂ and SCG_2.5%Ni_H₂ samples are classified as type Ib [45]. Both types Ia and Ib correspond to complete monolayer adsorption [46]. The uptake shows a fairly rapid increase with pressure until finally it reaches a plateau at a sufficiently high pressure [47]. In addition, type Ia isotherms define microporous materials in which there are mainly narrow micropores (width ~1 nm). Type Ib isotherms characterize materials with a pore size distribution, including wider micropores and possibly narrow mesopores (width ~2.5 nm) [47]. Figure 1b shows the adsorption isotherms for materials obtained by the hydrothermal method. According to the International Union for Pure and Applied Chemistry (IUPAC) classification, the isotherms obtained are type II related to unrestricted monolayer–multilayer adsorption. Type II isotherms correspond to lowporosity materials [47]. There is a hysteresis loop which can be classified as type H4. The H4 loop was associated with the filling of micro- and mesopores. In addition, the presence of micro- and mesopores in the catalysts obtained using the autoclave confirms the distribution of size pores.

The pore size distribution for Ni-modified catalysts measured by the physical N_2 adsorption was presented in Figure 2. Figure 2a shows the pore size distribution for the samples obtained by the impregnation and reduction in H_2 method, and Figure 2b for the samples obtained by the hydrothermal method in the autoclave.



Figure 2. Pore size distribution derived by applying the DFT method to N_2 adsorption–desorption isotherms determined at -196 °C for samples obtained by: (**a**) the impregnation method, and (**b**) the hydrothermal method in the autoclave.

Micropores in the range of 1-1.7 and mesopores in the range of 2-2.7 nm were mainly present in all samples obtained by the impregnation method. It was stated that the SCG_1%Ni_H₂ and SCG_2.5%Ni_H₂ samples showed significant differences in pore volume in the range of 2–3.5 nm in comparison to other samples. In addition, the $SCG_{2.5}$ Ni_H₂ sample showed the pore size distribution in the range of -5-5.5 nm. These results are consistent with the results obtained during textural studies (BET, Vtot, Vmic), isotherms of N_2 sorption, and pore size distribution. The catalysts obtained by the hydrothermal method were characterized by the presence of pores in the range of 1–2 nm, 2.4-3.1 nm and 5-5.7 nm (catalyst SCG_1%Ni_autoclave), 1-1.4 nm and 2.3-2.8 nm (catalyst SCG_2.5%Ni_autoclave), 1.4-2.1 nm and 3.4-3.8 nm (catalyst SCG_5%Ni_autoclave), 1.8 nm-2.5 nm, 3 nm-3.4 nm and 3.9 nm-4.5 nm (catalyst SCG_10%Ni_autoclave), and 2.8-3.7 nm and 5.2-5.9 nm (catalyst SCG_20%Ni_autoclave). For catalysts obtained by both methods and containing 5–20% Ni in the structure, significantly smaller pore volumes were recorded. This may indicate that the pores of the catalyst are clogged by the applied active phase. This effect has been previously reported in other works, and it was attributed to the blocking of pores [48].

X-ray diffractograms of the obtained nickel catalysts are depicted in Figure 3. For the carbon-based catalysts with 1–10 wt% of Ni in structures and obtained by the impregnation method (Figure 3a), the diffraction profiles exhibit two broad peaks at approximately $2\theta = 25^{\circ}$ and 43.5° , which are assigned to the reflection from (002) and (100) planes, respectively [49]. Moreover, broad peaks indicate an amorphous structure of the activated carbon support [20]. In addition, the reflection at $2\theta = 43.5^{\circ}$ may be assigned to NiO nanoparticles [50]. There is no noticeable difference in the XRD patterns between catalysts with 1–10 wt% Ni in their structures, which suggests that the method of impregnation with a reduction in H₂ and metal content (1–10 wt%) introduced into the carbon support has no significant effect on the structure of carbonaceous catalysts. Only the SCG_20%Ni_H₂ sample showed significant differences. According to JCPDS card 25-1044, this sample contained a NiCl₂ · 6H₂O compound with monoclinic crystallographic systems. Similar results were obtained by Yuan et al. [51].



Figure 3. XRD patterns of the catalysts prepared by: (**a**) the impregnation method, and (**b**) the hydrothermal method in the autoclave.

X-ray diffractograms of all samples obtained by the hydrothermal method (Figure 3b) showed the broad peaks at $2\theta = 25^{\circ}$ and 43° . This also indicated the amorphous carbon structure and was assigned to the activated carbon support [20]. For the catalysts with 2.5–20% Ni and obtained by the hydrothermal method, the presence of a sharp peak at $2\theta = 20^{\circ}$ was observed, and it was assigned to Ni(OH)₂ [52]. In addition, for the SCG_20%Ni_autoclave sample, two peaks around $2\theta = 37^{\circ}$ and 60° were observed, which were referred to as the diffraction peaks of NiO nanoparticles [53]. The results of the acid–base titration method, which was used to determine acid-site concentrations, are presented in Table 3.

 Table 3. Acid-site concentration determined using the acid-base titration method.

Sample	Acid-Site Concentration (mmol/g)
SCG_1%Ni_H ₂	1.738
SCG_2.5%Ni_H ₂	2.182
SCG_5%Ni_H ₂	2.588
SCG_10%Ni_H ₂	3.415
SCG_20%Ni_H ₂	4.522
SCG_1%Ni_autoclave	1.549
SCG_2.5%Ni_autoclave	1.222
SCG_5%Ni_autoclave	1.289
SCG_10%Ni_autoclave	1.157
SCG_20%Ni_autoclave	1.109

It is observable from Table 3 that for catalysts obtained by the impregnation method, the concentration of acid-sites increases with increases in nickel content in the catalyst, which may be related to the amount of active phase deposited on the carbon support. The highest concentration of acid-sites was determined for the SCG_20%Ni_H₂ sample, while the lowest concentration was determined for the SCG_1%Ni_H₂ sample. The active phase that influences the increase in the concentration of acid-sites was probably represented by NiCl₂ \cdot 6H₂O structures that were not reduced in the hydrogen flow. The presence of Ni and Cl in the catalysts was also confirmed by XRF analysis (Table 2). For catalysts obtained by the hydrothermal method, the concentration of acid-sites was determined for the reduced in the nickel content in the catalyst increases. The highest concentration of acid-sites was determined for the

SCG_1%Ni_autoclave sample, while the lowest concentration of acid-site was determined for the SCG_20%Ni_autoclave sample. It can be concluded that acid-site concentration was related to the presence of the active phase in the form of Ni(OH)₂. Considering the results of the titration method, it can be concluded that the lower concentrations of acid centers are related to the higher content of Ni(OH)₂ in the carbon carrier. The presence of nickel (II) hydroxide was confirmed using XRD analysis (Figure 3b).

Figure 4a,b show the spectra of the samples of the materials prepared in this study. FTIR spectra showed no significant differences in the presence of functional groups that could result from the use of different methods of synthesis of nickel catalysts. On the FTIR spectrum of all catalysts, the peaks around 3414 cm⁻¹ and 1632 cm⁻¹ were related to hydroxyl groups [54]. The peak at around of 1100 cm⁻¹ is characteristic of the C–O stretching frequency of the carboxylic and ether groups [55].



Figure 4. FTIR spectrum of catalysts obtained by: (**a**) the impregnation method, and (**b**) the hydrothermal method in the autoclave.

Morphologies of obtained catalysts were characterized with SEM analysis. The obtained results are shown in Figures 5 and 6.

The SEM images of all catalysts obtained by the impregnation method (Figure 5) show the surface of the carbon support, exhibiting some cracks and holes of various diameters and shapes [20,56]. The presence of white grains attached to the surface of the carbon support was also noted, which indicates the presence of Ni forms [57]. Furthermore, these structures were well distributed on the surface of the carbon support and only for the SCG_10%Ni_H₂ and SCG_20%Ni_H₂ samples were the grains agglomerated into larger spheres.

Figure 6 shows the morphology of material samples synthesized using the autoclave. The micrographs show the different structures of the catalysts in comparison to the catalysts prepared by the impregnation method, which are shown in Figure 5. Catalysts prepared by the hydrothermal method show a smoother and more regular surface compared to the impregnated catalysts. It has been successfully demonstrated in the literature that surface roughness is important for the activity of materials used in catalysis [58]. Karra et al. [59] observed that the chemical activity of catalysts with an irregular and rough surface structure was higher than the catalysts characterized by a smooth surface.







Figure 6. SEM micrographs of catalysts obtained by impregnation method: (**A**) SCG_1%Ni_autoclave, (**B**) SCG_2.5%Ni_autoclave, (**C**) SCG_5%Ni_autoclave, (**D**) SCG_10%Ni_autoclave, and (**E**) SCG_20%Ni_autoclave.

In addition, catalysts obtained by the hydrothermal method exhibited an irregular structure with a dominant flake form, just as found by Hou et al. [60]. These structures are most prominent for the SCG_20%Ni_autoclave sample (Figure 6E). As can be seen in Figure 6, these structures are densely distributed on the surface of the samples. In general, a good dispersion of nanostructures on the surface of the support is associated with the increased catalytic activity of the materials due to the availability of more catalytically active sites where the chemical reaction can take place [61,62]. Therefore, the close adhesion of nickel structures to each other may cause a decrease in the activity of catalysts obtained using the hydrothermal method compared to catalysts prepared using the impregnation method. In addition, the dense surface coverage of the carbon support by the active phase is also reflected in the parameters describing the porous structure (Table 1). It can be noted that the catalysts prepared by the impregnation method had significantly larger specific surface areas compared to the catalysts obtained by the hydrothermal method.

3.2. Activity of Carbon-Supported Nickel Catalysts

To evaluate the catalytic activity of the obtained catalysts, alpha-pinene oxidation process was carried out with the use of these materials.

In the first stage of catalytic tests, the activity of obtained catalysts was compared under the same conditions of preliminary tests (temperature 100 °C, reaction time 3 h, and catalyst content in the reaction mixture 1 wt%). The obtained results for catalysts prepared by impregnation are shown in Figure 7.



Figure 7. Comparison of selectivities of main products and alpha-pinene conversion after 3 h for the catalysts obtained by the impregnation and H_2 reduction method.

Among the catalysts obtained by the impregnation method, the SCG_5% Ni_H₂ sample was characterized by the highest catalytic activity, because the highest values of conversion of alpha-pinene and the sum of selectivity of the main reaction products (alpha-pinene oxide, verbenol, and verbenone) were achieved on this catalyst. The alpha-pinene conversion for this catalyst was 57 mol%. For the remaining catalysts, the conversion values amounted to 55 mol%, 41 mol%, 57 mol%, and 49 mol% (samples SCG_2.5% Ni_H₂, SCG_10% Ni_H₂, and SCG_20% Ni_H₂, respectively). For all catalysts, the main product formed with the highest selectivity was alpha-pinene oxide. Verbenol and verbenone were compounds formed in smaller amounts and with lower selectivity. For the SCG_5% Ni_H₂ sample, the selectivity of alpha-pinene oxide amounted to 26 mol%, verbenone 20 mol%, and verbenol 17 mol%. The sum of these selectivities was 63 mol%. For other catalysts, this sum was 54 mol% (for SCG_1% Ni_H₂), 59 mol% (for SCG_2.5% Ni_H₂), 51 mol% (for SCG_10% Ni_H₂), and 59 mol% (for SCG_20% Ni_H₂).

In addition, small amounts of compounds such as campholenic aldehyde, myrtenal, myrtenol, L-carveol, and trans-pinocarveol were also determined in the post-reaction mixtures.

The second stage of catalytic research concerned the determination of the most favorable conditions for the oxidation of alpha-pinene with the use of the most active catalyst. Considering the results obtained in the preliminary studies on the catalytic activity of carbon catalysts obtained by the impregnation method, the SCG_5%Ni_H₂ catalyst was selected for these tests. The following parameters were tested: catalyst content in the range of 0.1–5% wt%, temperature in the range of 90–110 °C, and reaction time from 10 to 300 min. The first parameter tested was the content of the SCG_5% Ni_H₂ catalyst in relation to the amount of alpha-pinene. The reaction was carried out at 100 °C and samples were taken after 3 h. The obtained results are shown in Figure 8.



Figure 8. Influence of the SCG_5%Ni_H₂ catalyst content on the selectivity of the main products and alpha-pinene conversion after 3 h.

Figure 8 shows that the change in the catalyst content in the reaction mixture in the range of 0.1–2.5 wt% does not significantly affect the alpha-pinene conversion values, while

for the catalyst content of 5 wt%, a significant decrease in alpha-pinene conversion (7 mol%) was visible. The highest selectivity of the transformation to alpha-pinene oxide was noted for the catalyst content of 0.5 wt%, and this value was 30 mol%. On the basis of the results presented in Figure 8, the amount of catalysts equal to 0.5 wt% was considered to be the most favorable.

Figure 9 shows the effect of the temperature of the alpha-pinene oxidation process on the selectivity of the main products and on the conversion of alpha-pinene. This step was carried out with the SCG_5% Ni_H₂ catalyst (its content was 0.5 wt%), and the sample of the post-reaction mixture (for GC analyses) was taken after 3 h.



Figure 9. Comparison of the selectivity of the main products and the conversion of alpha-pinene at different temperatures after 3 h and using the SCG_5%Ni_H₂ catalyst.

It is observable that as the temperature increases, the conversion of alpha-pinene increases to reach its maximum value (59 mol%) for the temperature of 110 °C. A slightly lower conversion value was recorded for the temperature of 100 °C, and it amounted to 57 mol%. For the temperature of 90 °C, a significant decrease in conversion was noted (20 mol%). The selectivity of the transformation of alpha-pinene to alpha-pinene oxide is the highest at 90 °C and it decreases with an increase in reaction temperature. For the temperature of 110 °C, an almost complete decrease in selectivity to alpha-pinene oxide (1 mol%) was observed. For all temperatures, as products formed with significant selectivity, apart from alpha-pinene oxide, verbenol and verbenone were noted (respectively: 15 mol% and 25 mol% for 90 °C, 15 mol% and 17 mol% for 100 °C, and 15 mol% and 29 mol%

for 110 °C). Considering both the value of alpha-pinene conversion and the selectivity of alpha-pinene oxide, the temperature of 100 °C was found to be the most favorable.

Figure 10 shows the effect of reaction time on alpha-pinene oxidation. For this stage of the studies, 8 g of alpha-pinene and 0.04 g of catalyst (0.5 wt%) were used. The temperature was 100 °C. The first sample of the reaction mixture for GC analyses was taken after 10 min, and the next ones were taken at intervals of 30 min until the reaction time of 300 min.



Figure 10. Influence of reaction time on the selectivity of the main products and alpha-pinene conversion using the SCG_5%Ni_H₂ catalyst.

The conversion of alpha-pinene increased during the prolongation of the reaction time, and it amounted to 61 mol% for the reaction time of 300 min. The selectivity of transformation to alpha-pinene oxide reached its maximum value for 120 min (33 mol%); after this time it decreased, and for the reaction time of 300 min it amounted to 2 mol%. The increase in the values of alpha-pinene conversion with a simultaneous decrease in the selectivity of the alpha-pinene oxide values indicates that the oxidation of alpha-pinene is replaced by the reactions in which alpha-pinene oxide undergoes other transformations (isomerization, dimerization, and polymerization). The main oxidation products of alpha-pinene and the exemplary products of follow-up reactions are shown in Figure 11 [63].



Figure 11. Main and follow-up products of alpha-pinene oxidation.

Figure 12 shows the catalytic activity of the catalysts obtained by the hydrothermal method under the conditions of the preliminary tests.



Figure 12. Comparison of selectivities of main products and alpha-pinene conversion after 3 h for the catalysts obtained by the hydrothermal method.

The most active catalyst from the materials obtained by the hydrothermal method was selected considering the values of conversion of alpha-pinene and the sum of the selectivity of the main reaction products.

During the studies for both the SCG_1%Ni_autoclave sample and the SCG_20%Ni_autoclave sample, the same alpha-pinene conversion value (51 mol%) was obtained. The catalyst containing 1 wt% of Ni in the structure was considered to be the most active because the highest sum of selectivity (75 mol%) of main reaction products (alpha-pinene oxide, verbenol, and verbenone) were achieved on this catalyst. For comparison, the sum of the selectivity of main reaction products for the SCG_20%Ni_autoclave sample was only 60 mol%. The sums of these selectivities for the other catalysts were, respectively: SCG_2.5% Ni_autoclave—61 mol%, SCG_5% Ni_autoclave—73 mol%, and SCG_10%Ni_autoclave—75 mol%. In addition, in the presence of the catalysts with 2.5–10 wt% Ni in their structure, the obtained conversion values were much lower: SCG_2.5% Ni_autoclave—38 mol%, SCG_5% Ni_autoclave—35 mol%, and SCG_10% Ni_autoclave—39 mol%.

Next, the catalytic studies concerned the determination of the most favorable conditions for the oxidation of alpha-pinene with the use of the SCG_1%Ni_autoclave catalyst. The following parameters were tested: catalyst content in the range of 0.1–5 wt%, temperature in the range of 90–110 °C, and reaction time from 10 to 300 min. The first parameter tested was the content of the SCG_1%Ni_autoclave catalyst in relation to the amount of alpha-pinene. The samples were taken after 3 h. The results of this step of the studies are shown in Figure 13.



Figure 13. Influence of the SCG_1%Ni_autoclave catalyst content on the selectivity of the main products and alpha-pinene conversion after 3 h.

Figure 13 shows that the change in the catalyst content in the reaction mixture in the range of 0.1–2.5 wt% does not significantly affect the alpha-pinene conversion values. For the catalyst content of 5 wt%, the largest decrease in alpha-pinene conversion (32 mol%) was observed. The highest selectivity of the transformation to alpha-pinene oxide was noted for the catalyst content of 0.5 wt%, and this value was 37 mol%. Based on the results presented in Figure 13, the amount of catalysts equal to 0.5 wt% was the most favorable.

Figure 14 shows the effect of temperature of the alpha-pinene oxidation process on the selectivity of the main products and on the conversion of alpha-pinene. This step was carried out with the SCG_1%Ni_autoclave catalyst (its content was 0.5 wt%), and the sample of the reaction mixture was taken for GC analyses after 3 h.



Figure 14. Comparison of the selectivity of the main products and the conversion of alpha-pinene at different temperatures after 3 h and using the SCG_1%Ni_autoclave catalyst.

It is observable that as the temperature increases, the conversion of alpha-pinene increases to reach its maximum value (51 mol%) for the temperature of 100 °C. The slightly lower conversion value was recorded for the temperature of 110 °C, and it amounted to 50 mol%. For the temperature of 90 °C, a significant decrease in conversion was noted (21 mol%). The selectivity of transformation to alpha-pinene oxide was the highest at 90 °C, and this value was 33 mol%. For the temperature of 110 °C, the decrease in selectivity of transformation to alpha-pinene oxide (24 mol%) was observed. For all temperatures, as products formed with significant selectivity, apart from alpha-pinene oxide, verbenol and verbenone were noted. Considering both the value of alpha-pinene conversion and

the selectivity to alpha-pinene oxide, the temperature of 100 $^{\circ}$ C was found to be the most favorable.

Figure 15 shows the effect of reaction time on the alpha-pinene oxidation process. For this stage of the research, 8 g of alpha-pinene and 0.04 g of catalyst (0.5 wt%) were used. The temperature was 100 $^{\circ}$ C. The first sample of the reaction mixture for GC analyses was taken after 10 min, and the next were taken at intervals of 30 min until the reaction time of 300 min.



Figure 15. Influence of reaction time on the selectivity of the main products and alpha-pinene conversion using the SCG_1%Ni_autoclave catalyst.

The conversion of alpha-pinene increased during the prolongation of the reaction time and amounted to 61 mol% for 300 min. The selectivity of alpha-pinene oxide reached its maximum value for the reaction time of 150 min (34 mol%); after this time, it decreased, and for the reaction time of 300 min it amounted to 8 mol%.

The comparison of the results of catalytic tests of the materials obtained by the two different methods shows that the materials obtained by the hydrothermal method were more active, taking into account the selectivity of alpha-pinene oxide (Figures 7 and 12), e.g., the comparison materials containing 1 wt% Ni shows that the use of the catalyst obtained by the hydrothermal method allows one to obtain about 80% higher selectivity of the transformation to alpha-pinene oxide at the similar value of conversion of alpha-pinene. For materials obtained by the impregnation method, the higher selectivity of the transformation of alpha-pinene to campholenic aldehyde, which is formed with several times higher selectivity in reactions with the participation of porous materials obtained by the impregnation method, is also noteworthy. This proves that part of the alpha-pinene

oxide formed in the process is isomerized to this compound, and this process takes place on the external surface of the catalyst, not in the pores. Among materials obtained by the method of impregnation followed by the reduction in hydrogen, the SCG_5%Ni_H₂ material was the most active. For the SCG_5%Ni_H₂ catalyst, the reaction under the most favorable conditions proceeded at 100 °C, at atmospheric pressure, with the catalyst content of 0.5 wt%, while the reaction time was 120 min. In these conditions, the conversion of alpha-pinene amounted to 35 mol%, and the selectivity of alpha-pinene oxide was 33 mol%. The catalytic studies with catalysts obtained by the hydrothermal method showed that the SCG_1%Ni_autoclave material was the most active. For this porous material, the reaction under the most favorable conditions also proceeded at 100 °C, at atmospheric pressure, with the catalyst content of 0.5 wt%, while the reaction time was 150 min. In these conditions, the conversion of alpha-pinene was 34 mol%, and the selectivity of alpha-pinene oxide was 34 mol%.

The comparison of the results of instrumental tests for materials that turned out to be the most active in alpha-pinene oxidation shows that the material obtained by the hydrothermal method was characterized by 60% lower acid-site concentration (Table 3) than the material obtained by the impregnation method, and yet it was more active. This difference is probably due to the location of the active centers—in the impregnated material, they are located only on the outer surface of the catalyst, while in the material obtained by the hydrothermal method, they are also located in the pores. The alpha-pinene oxide formed in the pores is probably more stable than the same compound but formed on external active sites, where it can more easily undergo subsequent reactions. Therefore, the use of the material obtained by the hydrothermal method as the catalyst, but containing less nickel, is more advantageous—the narrow space in the pores provides greater stability in forming the epoxide compound. Comparing the pore size of materials obtained by two different methods (Figure 2a,b), it can be seen that the most active catalyst obtained by the hydrothermal method has pores of 1.8–1.9 nm, which are not present in any other obtained materials. It is most likely that pores of this size determine the greater activity of the SCG_1%Ni_autoclave material.

3.3. Determination of the Kinetics Parameters Determination of the Kinetics Parameters

These kinetic studies explore the alpha-pinene oxidation over sample SCG_1% Ni_autoclave. A series of experiments was performed in which the influence of the various parameters on the reaction rate was checked: temperature, reaction time, and amount of catalyst. One assumption was made, i.e., the oxygen uptake (expressed in mol/dm³) was constant during all experiments, and simultaneously the oxygen uptake/alpha-pinene ratio (defined in mol_{O2·molα-pinene}) was changing. In these conditions, the reaction mixture composition was determined for each temperature (90 °C, 100 °C, and 110 °C; P_{O2} = 1 bar). The kinetic curves were differentiated to calculate the alpha-pinene oxidation rates. It was observed that the turbulence generated near the catalyst particles by a vigorous stirring of the reaction mixture was helpful in eliminating the external diffusion resistance between the bulk liquid and the surface of the catalyst. Internal diffusion resistance was also insignificant because of the small size of catalyst particles. It was evidenced that the product content slightly depends on the oxygen uptake/alpha-pinene ratio. Furthermore, the alpha-pinene oxidation rate increases along with the increase in the oxidation temperature.

Activation energy calculated from Arrhenius dependence was $89.2 \pm 3.4 \text{ kJ/mol}$, and the effective kinetic constant was $k_{eff} = 1.0 \times 10^{10} \text{ mol} \, {}^{0.5} \text{.dm}^{-1.5} \text{.min}^{-1}$. The model fits the experimental data very well (the regression coefficient equals 0.9163). Therefore, under the reaction conditions, the reaction rate of alpha-pinene oxidation by molecular oxygen can be described as follows:

$$R_{\rm O} = k_{eff} \cdot f(concentration)^{0.5} \cdot P^0_{\rm O2} \cdot exp(-E_a/RT) [mol.dm^{-3} \cdot min^{-1}]$$

The estimated activation energy is in accordance with typical values of activation energy for alpha-pinene oxidation by molecular oxygen (81.3 kJ/mol) [64], for alpha-pinene

oxidation over FeCl₃-modified carbonaceous catalysts from orange peels (92.7 kJ/mol) [43], for cis-pinene oxidation (79.5 kJ/mol) [65], and dibenzyl ester oxidation initiated by azoisobutyronitrile (93.66 kJ/mol) [66].

4. Conclusions

This work described the simple method for processing food industry waste—coffee grounds—for which disposal and safe storage are still a challenge for waste management entities. Considering the presented results, it can be concluded that coffee grounds can be an excellent raw material for obtaining activated carbons, which can be used as catalyst supports. An example of such application of activated carbons obtained from coffee grounds can be their modification with nickel salts. In this way, it was possible to obtain cheap catalysts that were active in the oxidation of alpha-pinene. As a result of two different methods of synthesis of carbon catalysts, two groups of catalytically active materials were obtained, which differed in their physical and chemical properties. Among the catalysts obtained using the method of impregnation followed by the reduction in hydrogen, SCG_5%Ni_H₂ material was the most active; among the catalysts obtained by the hydrothermal method, SCG_1%Ni_autoclave material was the most active. With the SCG_5%Ni_H₂ catalyst, the reaction under the most favorable conditions proceeded at 100 °C, at atmospheric pressure, and with the catalyst content of 0.5 wt%, while the reaction time was 120 min. In these conditions, the conversion of alpha-pinene was 35 mol%, and the selectivity of transformation to alpha-pinene oxide was 33 mol%. With the SCG_1%Ni_autoclave catalyst, the reaction under the most favorable conditions was also carried out at 100 °C, at atmospheric pressure, with the catalyst content of 0.5 wt% and for 150 min. At these mild process conditions, the conversion of alpha-pinene was 34 mol%, and the selectivity of transformation to the main product (alpha-pinene oxide) was 34 mol%.

Considering the nickel content of the carbon support, it can be concluded that the hydrothermal method is the better synthesis method in terms of economy, as it allows one to obtain the catalyst with a much lower nickel content (1 wt% Ni) and with similar catalytic activity in comparison to the catalyst obtained by the impregnation method (5 wt% Ni). In addition, our research indicates that alpha-pinene oxide formed in the pores of the catalyst is likely to be more stable than the same compound formed on external active sites, where it can more easily undergo subsequent reactions. Therefore, the use of the material obtained by the hydrothermal method as the catalyst, but containing a lesser amount of nickel, is more advantageous—the narrow space in the pores provides greater stability to the formed epoxide compound. At the same time, our research shows that the pore size of materials obtained by the hydrothermal method and used in the alpha-pinene oxidation process may be of great importance for the final oxidation results—the most active catalyst obtained in our research using the hydrothermal method had pores of 1.8–1.9 nm, which were not found in any other material obtained in this work. It can therefore be assumed that it is most likely that pores of this size determine the greater activity of the material named SCG_1%Ni_autoclave.

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References

- Reza, M.S.; Yun, C.S.; Afroze, S.; Radenahmad, N.; Bakar, M.S.A.; Saidur, R.; Taweekun, J.; Azad, A.K. Preparation of Activated Carbon from Biomass and Its' Applications in Water and Gas Purification, a Review. *Arab J. Basic Appl. Sci.* 2020, 27, 208–238. [CrossRef]
- 2. Yahya, M.A.; Al-Qodah, Z.; Ngah, C.W.Z. Agricultural Bio-Waste Materials as Potential Sustainable Precursors Used for Activated Carbon Production: A Review. *Renew. Sustain. Energy Rev.* **2015**, *46*, 218–235. [CrossRef]
- 3. Kiełbasa, K.; Kamińska, A.; Niedoba, O.; Michalkiewicz, B. CO₂ Adsorption on Activated Carbons Prepared from Molasses: A Comparison of Two and Three Parametric Models. *Materials* **2021**, *14*, 7458. [CrossRef] [PubMed]
- 4. Adeyi, O. Proximate Composition of Some Agricultural Wastes in Nigeria and Their Potential Use in Activated Carbon Production. *J. Appl. Sci. Environ. Manag.* **2010**, *14*, 55–58. [CrossRef]
- 5. González-García, P. Activated Carbon from Lignocellulosics Precursors: A Review of the Synthesis Methods, Characterization Techniques and Applications. *Renew. Sustain. Energy Rev.* **2018**, *82*, 1393–1414. [CrossRef]
- 6. Kim, M.H.; Jeong, I.T.; Park, S.B.; Kim, J.W. Analysis of Environmental Impact of Activated Carbon Production from Wood Waste. *Environ. Eng. Res.* 2019, 24, 117–126. [CrossRef]
- Danish, M.; Ahmad, T. A Review on Utilization of Wood Biomass as a Sustainable Precursor for Activated Carbon Production and Application. *Renew. Sustain. Energy Rev.* 2018, 87, 1–21. [CrossRef]
- 8. Zieliński, B.; Miądlicki, P.; Przepiórski, J. Development of Activated Carbon for Removal of Pesticides from Water: Case Study. *Sci. Rep.* 2022, 12, 20869. [CrossRef]
- 9. Mussatto, S.I.; Carneiro, L.M.; Silva, J.P.A.; Roberto, I.C.; Teixeira, J.A. A Study on Chemical Constituents and Sugars Extraction from Spent Coffee Grounds. *Carbohydr. Polym.* **2011**, *83*, 368–374. [CrossRef]
- 10. Janissen, B.; Huynh, T. Chemical Composition and Value-Adding Applications of Coffee Industry by-Products: A Review. *Resour. Conserv. Recycl.* 2018, 128, 110–117. [CrossRef]
- 11. Low, J.H.; Rahman, W.A.W.A.; Jamaluddin, J. Structural Elucidation of Tannins of Spent Coffee Grounds by CP-MAS 13C NMR and MALDI-TOF MS. *Ind. Crops Prod.* 2015, 69, 456–461. [CrossRef]
- 12. De Nicola, E.; Meriç, S.; Gallo, M.; Iaccarino, M.; Della Rocca, C.; Lofrano, G.; Russo, T.; Pagano, G. Vegetable and Synthetic Tannins Induce Hormesis/Toxicity in Sea Urchin Early Development and in Algal Growth. *Environ. Pollut.* **2007**, *146*, 46–54. [CrossRef]
- 13. Mohanpuria, P.; Yadav, S.K. Retardation in Seedling Growth and Induction of Early Senescence in Plants upon Caffeine Exposure Is Related to Its Negative Effect on Rubisco. *Photosynthetica* **2009**, *47*, 293–297. [CrossRef]
- 14. Miyashira, C.H.; Tanigushi, D.G.; Gugliotta, A.M.; Santos, D.Y. Influence of Caffeine on the Survival of Leaf-Cutting Ants Atta Sexdens Rubropilosa and in Vitro Growth of Their Mutualistic Fungus. *Pest Manag. Sci.* **2012**, *68*, 935–940. [CrossRef]
- 15. Sledz, W.; Los, E.; Paczek, A.; Rischka, J.; Motyka, A.; Zoledowska, S.; Piosik, J.; Lojkowska, E. Antibacterial Activity of Caffeine against Plant Pathogenic Bacteria. *Acta Biochim. Pol.* **2015**, *62*, 605–612. [CrossRef]
- Tsou, M.F.; Hung, C.F.; Lu, H.F.; Wu, L.T.; Chang, S.H.; Chang, H.L.; Chen, G.W.; Chung, J.G. Effects of Caffeic Acid, Chlorogenic Acid and Ferulic Acid on Growth and Arylamine N-Acetyltransferase Activity in Shigella Sonnei (Group D). *Microbios* 2000, 101, 37–46.
- 17. Woldesenbet, A.G.; Woldeyes, B.; Chandravanshi, B.S. Bio-Ethanol Production from Wet Coffee Processing Waste in Ethiopia. *Springerplus* **2016**, *5*, 1903. [CrossRef]
- Adi, A.J.; Noor, Z.M. Waste Recycling: Utilization of Coffee Grounds and Kitchen Waste in Vermicomposting. *Bioresour. Technol.* 2009, 100, 1027–1030. [CrossRef]
- 19. Mussatto, S.I.; Machado, E.M.S.; Carneiro, L.M.; Teixeira, J.A. Sugars Metabolism and Ethanol Production by Different Yeast Strains from Coffee Industry Wastes Hydrolysates. *Appl. Energy* **2012**, *92*, 763–768. [CrossRef]
- Kamińska, A.; Miądlicki, P.; Kiełbasa, K.; Kujbida, M.; Sreńscek-Nazzal, J.; Wróbel, R.J.; Wróblewska, A. Activated Carbons Obtained from Orange Peels, Coffee Grounds, and Sunflower Husks—Comparison of Physicochemical Properties and Activity in the Alpha-Pinene Isomerization Process. *Materials* 2021, 14, 7448. [CrossRef]
- Shanthilal, J.; Bhattacharya, S. Nanoparticles and Nanotechnology in Food. In *Conventional and Advanced Food Processing Technologies*; John Wiley & Sons, Ltd.: Chichester, UK, 2014; Volume 9781118406, pp. 567–594. ISBN 9781118406281.
- Ádám, A.A.; Szabados, M.; Varga, G.; Papp, Á.; Musza, K.; Kónya, Z.; Kukovecz, Á.; Sipos, P.; Pálinkó, I. Ultrasound-Assisted Hydrazine Reduction Method for the Preparation of Nickel Nanoparticles, Physicochemical Characterization and Catalytic Application in Suzuki-Miyaura Cross-Coupling Reaction. *Nanomaterials* 2020, 10, 632. [CrossRef] [PubMed]
- 23. Iqbal, P.; Preece, J.A.; Mendes, P.M. Nanotechnology: The "Top-Down" and "Bottom-Up" Approaches. In *Supramolecular Chemistry*; John Wiley & Sons, Ltd.: Chichester, UK, 2012.
- 24. Xie, Y.; Kocaefe, D.; Chen, C.; Kocaefe, Y. Review of Research on Template Methods in Preparation of Nanomaterials. *J. Nanomater.* **2016**, 2016, 1–10. [CrossRef]
- 25. Lestinsky, P.; Zikmund, Z.; Grycova, B.; Ryczkowski, R.; Grams, J.; Inayat, A. Production of Hydrogen over Ni/Carbonaceous Catalyst. *Fuel* **2020**, *278*, 118398. [CrossRef]

- 26. Fidalgo, B.; Zubizarreta, L.; Bermúdez, J.M.; Arenillas, A.; Menéndez, J.A. Synthesis of Carbon-Supported Nickel Catalysts for the Dry Reforming of CH4. *Fuel Process. Technol.* **2010**, *91*, 765–769. [CrossRef]
- Malobela, L.J.; Heveling, J.; Augustyn, W.G.; Cele, L.M. Nickel-Cobalt on Carbonaceous Supports for the Selective Catalytic Hydrogenation of Cinnamaldehyde. *Ind. Eng. Chem. Res.* 2014, 53, 13910–13919. [CrossRef]
- Li, B.; Ren, Y.; Fan, Q.; Feng, A.; Dong, W. Preparation and Characterization of Spherical Nickel-Doped Carbonaceous Resin as Hydrogenation Catalysts I. Carbonization Procedures. *Carbon* 2004, 42, 2669–2676. [CrossRef]
- Salimi, M.; Tavasoli, A.; Balou, S.; Hashemi, H.; Kohansal, K. Influence of Promoted Bimetallic Ni-Based Catalysts and Micro/Mesopores Carbonaceous Supports for Biomass Hydrothermal Conversion to H2-Rich Gas. *Appl. Catal. B Environ.* 2018, 239, 383–397. [CrossRef]
- Altass, H.M.; Ahmed, S.A.; Salama, R.S.; Moussa, Z.; Jassas, R.S.; Alsantali, R.I.; Al-Rooqi, M.M.; Ibrahim, A.A.; Khder, M.A.; Morad, M.; et al. Low Temperature CO Oxidation Over Highly Active Gold Nanoparticles Supported on Reduced Graphene Oxide@Mg-BTC Nanocomposite. *Catal. Lett.* 2022, 153, 876–886. [CrossRef]
- Masruri; Pamungkas, K.K. Copper Nanoparticle Catalysed Aerobic Oxidation of α-Pinene. IOP Conf. Ser. Mater. Sci. Eng. 2019, 546, 042023. [CrossRef]
- Lei, J.; Lu, X.H.; Zhang, J.L.; Wei, X.L.; Zhou, D.; Xia, Q.H. Epoxidation of Mixed Bi-Olefins with Air over Nanosized Co 3O4 Assisted by Ultrasonic Waves. Indian J. Chem. Sect. A Inorg. Phys. Theor. Anal. Chem. 2013, 52, 709–716.
- Kamińska, A.; Maciejewska, N.; Miądlicki, P.; Kiełbasa, K.; Sreńscek-Nazzal, J.; Michalkiewicz, B. Fe-Modified Activated Carbon Obtained from Biomass as a Catalyst for α-Pinene Autoxidation. *Polish J. Chem. Technol.* 2021, 23, 73–80. [CrossRef]
- 34. Rauchdi, M.; Ait Ali, M.; Roucoux, A.; Denicourt-Nowicki, A. Novel Access to Verbenone via Ruthenium Nanoparticles-Catalyzed Oxidation of A-Pinene in Neat Water. *Appl. Catal. A Gen.* **2018**, 550, 266–273. [CrossRef]
- 35. Cánepa, A.L.; Chanquía, C.M.; Vaschetti, V.M.; Eimer, G.A.; Casuscelli, S.G. Biomass toward Fine Chemical Products: Oxidation of α-Pinene over Sieves Nanostructured Modified with Vanadium. *J. Mol. Catal. A Chem.* **2015**, 404–405, 65–73. [CrossRef]
- Denicourt-Nowicki, A.; Roucoux, A. Odyssey in Polyphasic Catalysis by Metal Nanoparticles. *Chem. Rec.* 2016, 16, 2127–2141. [CrossRef]
- 37. Zhu, S.J.; Xu, S.C.; Zhao, Z.D. An Efficient Synthesis Method Targeted to a Novel Aziridine Derivative of P-Menthane from Turpentine and Its Herbicidal Activity. *Nat. Prod. Res.* **2017**, *31*, 1536–1543. [CrossRef]
- Yoo, S.K.; Day, D.F. Bacterial Metabolism of α- and β-Pinene and Related Monoterpenes by Pseudomonas Sp. Strain PIN. *Process Biochem.* 2002, *37*, 739–745. [CrossRef]
- Ali, B.; Al-Wabel, N.A.; Shams, S.; Ahamad, A.; Khan, S.A.; Anwar, F. Essential Oils Used in Aromatherapy: A Systemic Review. *Asian Pac. J. Trop. Biomed.* 2015, 5, 601–611. [CrossRef]
- 40. Wender, P.A.; Mucciaro, T.P. A New and Practical Approach to the Synthesis of Taxol and Taxol Analogues: The Pinene Path. J. Am. Chem. Soc. **1992**, 114, 5878–5879. [CrossRef]
- Alshorifi, F.T.; Tobbala, D.E.; El-Bahy, S.M.; Nassan, M.A.; Salama, R.S. The Role of Phosphotungstic Acid in Enhancing the Catalytic Performance of UiO-66 (Zr) and Its Applications as an Efficient Solid Acid Catalyst for Coumarins and Dihydropyrimidinones Synthesis. *Catal. Commun.* 2022, 169, 106479. [CrossRef]
- 42. Ananikov, V.P. Nickel: The "Spirited Horse" of Transition Metal Catalysis. ACS Catal. 2015, 5, 1964–1971. [CrossRef]
- Kamińska, A.; Miądlicki, P.; Kiełbasa, K.; Serafin, J.; Sreńscek-Nazzal, J.; Wróbel, R.J.; Wróblewska, A. FeCl3-Modified Carbonaceous Catalysts from Orange Peel for Solvent-Free Alpha-Pinene Oxidation. *Materials* 2021, 14, 7729. [CrossRef] [PubMed]
- 44. Dongil, A.B.; Ghampson, I.T.; García, R.; Fierro, J.L.G.; Escalona, N. Hydrodeoxygenation of Guaiacol over Ni/Carbon Catalysts: Effect of the Support and Ni Loading. *RSC Adv.* **2016**, *6*, 2611–2623. [CrossRef]
- 45. Rahman, M.M.; Muttakin, M.; Pal, A.; Shafiullah, A.Z.; Saha, B.B. A Statistical Approach to Determine Optimal Models for IUPAC-Classified Adsorption Isotherms. *Energies* **2019**, *12*, 4565. [CrossRef]
- Sing, K. The Use of Nitrogen Adsorption for the Characterisation of Porous Materials. *Colloids Surf. A Physicochem. Eng. Asp.* 2001, 187–188, 3–9. [CrossRef]
- Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* 2015, 87, 1051–1069. [CrossRef]
- Pastor-Pérez, L.; Buitrago-Sierra, R.; Sepúlveda-Escribano, A. CeO₂-Promoted Ni/Activated Carbon Catalysts for the Water-Gas Shift (WGS) Reaction. *Int. J. Hydrog. Energy* 2014, 39, 17589–17599. [CrossRef]
- Sreńscek-Nazzal, J.; Kamińska, A.; Miądlicki, P.; Wróblewska, A.; Kiełbasa, K.; Wróbel, R.J.; Serafin, J.; Michalkiewicz, B. Activated Carbon Modification towards Efficient Catalyst for High Value-Added Products Synthesis from Alpha-Pinene. *Materials* 2021, 14, 7811. [CrossRef]
- 50. Iwu, K.O.; Lombardo, A.; Sanz, R.; Scirè, S.; Mirabella, S. Facile Synthesis of Ni Nanofoam for Flexible and Low-Cost Non-Enzymatic Glucose Sensing. *Sens. Actuators B Chem.* **2016**, 224, 764–771. [CrossRef]
- Yuan, G.; Jiang, Z.; Aramata, A.; Gao, Y. Electrochemical Behavior of Activated-Carbon Capacitor Material Loaded with Nickel Oxide. *Carbon* 2005, 43, 2913–2917. [CrossRef]
- Peck, M.A.; Langell, M.A. Comparison of Nanoscaled and Bulk NiO Structural and Environmental Characteristics by XRD, XAFS, and XPS. Chem. Mater. 2012, 24, 4483–4490. [CrossRef]

- 53. Kalam, A.; Al-Sehemi, A.G.; Al-Shihri, A.S.; Du, G.; Ahmad, T. Synthesis and Characterization of NiO Nanoparticles by Thermal Decomposition of Nickel Linoleate and Their Optical Properties. *Mater. Charact.* **2012**, *68*, 77–81. [CrossRef]
- 54. Rahdar, A.; Aliahmad, M.; Azizi, Y. NiO Nanoparticles: Synthesis and Characterization. J. Nanostruct. 2015, 5, 145–151. [CrossRef]
- 55. O'Reilly, J.M.; Mosher, R.A. Functional Groups in Carbon Black by FTIR Spectroscopy. *Carbon* **1983**, *21*, 47–51. [CrossRef]
- Kemp, K.C.; Baek, S.B.; Lee, W.G.; Meyyappan, M.; Kim, K.S. Activated Carbon Derived from Waste Coffee Grounds for Stable Methane Storage. *Nanotechnology* 2015, 26, 385602. [CrossRef]
- 57. Afriani, A.; Abdullah, I.; Krisnandi, Y.K. Synthesis of NiCl₂ impregnated Mesoporous Carbon and Its Adsorption Activity on CO₂. In Proceedings of the AIP Conference Proceedings, Bandung, Indonesia, 29–30 September 2021; Volume 2349, p. 020048.
- 58. Cuenya, B.R. Synthesis and Catalytic Properties of Metal Nanoparticles: Size, Shape, Support, Composition, and Oxidation State Effects. *Thin Solid Film.* **2010**, *518*, 3127–3150. [CrossRef]
- 59. Karra, S.; Wooten, M.; Griffith, W.; Gorski, W. Morphology of Gold Nanoparticles and Electrocatalysis of Glucose Oxidation. *Electrochim. Acta* **2016**, *218*, 8–14. [CrossRef]
- Hou, J.; Jiang, K.; Wei, R.; Tahir, M.; Wu, X.; Shen, M.; Wang, X.; Cao, C. Popcorn-Derived Porous Carbon Flakes with an Ultrahigh Specific Surface Area for Superior Performance Supercapacitors. *ACS Appl. Mater. Interfaces* 2017, *9*, 30626–30634. [CrossRef]
 Name M. M.; K.; Wei, R.; Tahir, M.; Wu, X.; Shen, M.; Wang, X.; Cao, C. Popcorn-Derived Porous Carbon Flakes with an Ultrahigh Specific Surface Area for Superior Performance Supercapacitors. *ACS Appl. Mater. Interfaces* 2017, *9*, 30626–30634. [CrossRef]
- 61. Narayan, N.; Meiyazhagan, A.; Vajtai, R. Metal Nanoparticles as Green Catalysts. *Materials* **2019**, *12*, 3602. [CrossRef]
- Ma, Q.; Zhang, Y.; Zhu, X.; Chen, B. Hollow Multi-Shelled Co₃O₄ as Nanoreactors to Activate Peroxymonosulfate for Highly Effective Degradation of Carbamazepine: A Novel Strategy to Reduce Nano-Catalyst Agglomeration. *J. Hazard. Mater.* 2022, 427, 127890. [CrossRef]
- Sekimoto, K.; Fukuyama, D.; Inomata, S. Accurate Identification of Dimers from α-Pinene Oxidation Using High-Resolution Collision-Induced Dissociation Mass Spectrometry. J. Mass Spectrom. 2020, 55, e4508. [CrossRef]
- 64. Da Silva, M.J.; Robles-Dutenhefner, P.; Menini, L.; Gusevskaya, E.V. Cobalt Catalyzed Autoxidation of Monoterpenes in Acetic Acid and Acetonitrile Solutions. *J. Mol. Catal. A Chem.* **2003**, 201, 71–77. [CrossRef]
- Ancel, J.E.; Maksimchuk, N.V.; Simakova, I.L.; Semikolenov, V.A. Kinetic Peculiarities of α-Pinene Oxidation by Molecular Oxygen. *Appl. Catal. A Gen.* 2004, 272, 109–114. [CrossRef]
- 66. Emanuel, N.M.; Knorre, D.G. Kurs Khimicheskoi Kinetiki (Course in Chemical Kinetics); Vysshaya Shkola: Moscow, Russia, 1962.

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