Fe-modified activated carbon obtained from biomass as a catalyst for α-pinene autoxidation

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The presented work describes the autoxidation of alpha-pinene for the first time using a catalyst based on activated carbon from biomass with introduced Fe. The raw material for the preparation of the carbon material was waste orange peel, which was activated with a KOH solution. The following instrumental methods characterized the obtained catalyst (Fe/O_AC): N2 adsorption at 77 K, XRD, UV, SEM, TEM, X-ray microanalysis, and catalytic studies. It was shown that the Fe/O_AC catalyst was very active in the autoxidation of alpha-pinene. The main reaction products were: alpha-pinene oxide, verbenone, verbenol, and campholenic aldehyde.

Keywords: activated carbon, carbonaceous catalysts, autoxidation, alpha-pinene, iron particles, biomass.

INTRODUCTION

The preparation of carbon materials from inexpensive and widely available precursors, such as waste biomass from the food industry, has become the main topic of interest in new material research1-3. The development of a method of synthesizing carbon materials from biomass enables the use and management of waste, the disposal of which and environmentally safe storage for it has been problematic4.

Productions of many different carbonaceous materials have been developed e.g. carbon spheres5,6, hierarchical porous carbon nanosheets7, exfoliated graphitic carbon nitride8, TiO2-loaded carbon fiber cloths9, hybrid carbon-TiO2 sphere10, TiO2-reduced graphene oxide11,12, carbon nanotubes13,14, nano carbon black13, activated carbon15-19. Carbonaceous materials have found a multifunctional application in the fields of catalysis20-28, photocatalysis8,9,12,29 water treatment30, supercapacitors7, energy storage30, electrochemical sensor13, sorption5,16,18,19,31 and so on.

The cultivation of citrus trees is considered to be the most developing agricultural sector in recent years. The citrus fruit grown on the most significant scale is the sweet orange (Citrus sinensis), which accounts for up to 70% of citrus fruits' total production and consumption32. These fruits are processed on an industrial scale into juices, jams, and marmalades33. It is estimated that the citrus fruit processing industry generates nearly 40 tons of waste annually, a significant proportion (~65%) of orange peels34. The high content of organic matter in the orange peel makes it challenging to dispose of it quickly because it affects the bacterial flora of the soil. The storage of such waste requires neutralizing the acidic pH of this biomass35. The demand for fresh orange juices and citrus preserves is constantly growing, so it is so important to minimize waste during production. Converting waste biomass to carbonaceous materials helps lower the production costs of activated carbons and is a potentially more economical alternative to available commercial carbons36. However, before turning waste orange peels into carbonaceous materials, they can be used to extract a very valuable terpene compound: limonene. Limonene itself and its oxidation as well isomerization products have many applications in organic synthesis and the cosmetics, food, perfumery, and cosmetics industries37-43.

The preparation of activated carbons from orange peels on a laboratory scale is of interest to many researchers. Chen et al.44 described the preparation of activated carbons from orange peels by pyrolysis at various temperatures and with limited oxygen supply. The carbons obtained in this way can be used as adsorbents for removing toxic compounds from the environment, e.g., naphthalene and 1-naphthol. Giraldo et al.45 reported the preparation of catalysts prepared by coating with a layer of TiO2 activated carbon obtained from orange peel. In the biomass impregnation cell, KOH was used as a chemical activator, and the pyrolysis of the carbonaceous substrate was carried out in a vertical tubular reactor at 550°C. The resulting material was then coated with titanium dioxide and used in the NOx decomposition. Dhorange46 described the synthesis of activated carbons from orange peels, which was a waste product from a local marketplace. The researchers used orthophosphoric acid as a chemical activator and then heated the impregnated biomass in a muffle furnace at 350°C. Another team of scientists described the pyrolysis of orange peel in a carbon dioxide environment47. Biomass pyrolysis was carried out in a tubular reactor, the flow of N2 and CO2 was 300 ml/min, and the temperature range was from 200°C to 700°C. Hui Pan et al.48 reported the preparation of sulfonated carbons from fresh orange peels by partial hydrothermal carbonization. Concentrated sulfuric acid(VI) was used for chemical activation. The materials obtained in this way were active in the esterification of oleic and citric acids.

Alpha-pinene is a cyclic compound from the group of monoterpenes. This compound can be obtained from turpentine obtained from pine tree resin49. Alpha-pinene occurs in nature as a mixture of two enantiomers, the content of which in the mixture may vary depending on the species, age of the tree, and the tissue from which it was obtained (e.g., a needle or xylem)50,51. This compound is used extensively in the perfumery, cosmetics, food, and pharmaceutical industries52. This compound is used extensively in the perfumery, cosmetics, food, and pharmaceutical industries. In addition to industrial applications, this compound also exhibits anti-inflammatory,
antibacterial, antiseptic, and anti-cancer properties. Alpha-pinene has also been used as a valuable substrate in organic syntheses (oxidation (including autoxidation) and isomerization reactions).

There are two ways of conducting the alpha-pinene autoxidation process: autoxidation without the presence of catalysts or with the use of catalysts. In the first step, the reactions were carried out at 100°C using oxygen and without the presence of light. The main products of this reaction were oxygen derivatives such as alpha-foam, verbenone, and myrtenal. The autoxidation of alpha-pinene, which required the use of catalysts, was carried out in the temperature range of 65–90°C. Metal-modified catalysts (Cr, Co, Cu) were used in the reaction. The main products that were obtained during this reaction were alpha-pinene oxide, verbenol, and verbenone.

Currently, conducting catalytic reactions in the presence of catalysts is at the center of interest of scientists dealing with catalytic processes. CoCl₂ in the presence of oxygen, acetic acid, and acetonitrile as a solvent was used to carry out the catalytic autoxidation of alpha-pinene. The main products were alpha-pinene oxide, alpha-campfolaldehyde, and verbenol and transverbenol. The highest selectivity was recorded for alpha-pinene oxide, and it was 31%, and trans-verbenol 21%, and also for verbenone 26%. 55% alpha-pinene conversion was achieved. In another work, Mao et al. used the Fe(III)/SiO₂ composite as the catalyst. The reaction was carried out in the presence of pure oxygen and using acetonitrile as the solvent. The main products were α-pinene oxide (selectivity was 21%), verbenol (selectivity 45%), and verbenone (selectivity 18%), and the α-pinene conversion was 73%. Gomes et al. carried out alpha-pinene autoxidation reactions using a Co(OAc)₂/bromide catalyst. The main reaction products were cis-verbenyl, verbenone, and myrtenal. The selectivities of the main products were 30%, 20%, and 10% respectively.

Preparation Fe/O_AC

To apply the iron particles on the carbon surface, 1 g of activated carbon (O_AC) was weighed and suspended in 400 ml of iron salt solution (7.8 g FeCl₃ x 6H₂O and 3.8 g FeSO₄·7H₂O) and then placed on a magnetic stirrer. Then the carbon solution was heated on a magnetic stirrer (700 rpm) to 80°C and kept at this temperature for 90 minutes. After this time, 5M NaOH solution was added dropwise to the material until the pH was about 11, and then it was left on a magnetic stirrer at 80°C, 700 rpm for 1 hour. After impregnation was completed, the sample was removed from the magnetic stirrer and left in the flask for 24 hours at ambient temperature. The material was poured with distilled water until the filtrate pH was constant – about 7. The obtained activated carbon was designated as O_AC.

Alpha-pinene autoxidation

The reaction of alpha-pinene autoxidation was carried out in a glass reactor with a capacity of 5 cm³, equipped with a reflux condenser and a stirrer. The flask was placed in an oil bath set on a magnetic stirrer with a heating function. 2 g of alpha-pinene (98%, Aldrich) was used for the autoxidation studies. The catalyst activity was tested under the following conditions: the reaction temperature range was 70–120°C, the amount of the catalyst was 0.5–5 wt.%. Samples were taken after 2 hours and 24 hours. The most favorable conditions were determined.

**Figure 1.** Main products of alpha-pinene autoxidation
based on the conversion and selectivity of alpha-pinene oxide. Other products determined during the tests were: verbenone, verbolen, and campholenic aldehyde (Fig. 1).

To perform the quantitative analysis, the reaction mixture was centrifuged and dissolved in acetone in a weight ratio of 1:10. The quantitative analysis was performed with a Thermo Electron FOCUS chromatograph equipped with an FID detector and a ZB-1701 column (30m x 0.53mm x 1um). The operating parameters of the chromatograph were as follows: helium flow 1.2 ml/min, injector temperature 220°C, detector temperature 250°C, furnace temperature isothermally for 2 minutes at 50°C, increase at a rate of 6°C/min to 120°C, at 120°C isothermally for 4 min, then rising at 15°C/min to 240°C. To determine the composition of post-reaction mixtures, the method of internal normalization was used.

Characterization

For textural characterization was used ASAP Sorption Surface Area and Pore SizeAnalyzer. Nitrogen adsorption isotherm was measured at −196°C. Before adsorption measurements sample was outgassed at 250°C for 19 hours. The specific surface area was calculated using the Brunauer–Emmett–Teller (SBET) equation from nitrogen adsorption isotherms. The total pore volume (Vtov) was evaluated from the nitrogen volume adsorbed at a relative pressure of ~0.98. The volumes of micropores were calculated by the DFT method based on nitrogen adsorption. The pore size distribution (Vmes(N2)) was obtained from the DFT model in the ASAP 2460 Version 3.01 software package based on the N2 sorption isotherm. DFT used: N2 at 77 K on carbon (slit N2-DFT Model adsorption).

The morphology of the sample was observed via scanning electron microscopy with cold emission (UHR FE-SEM Hitachi SU8020). The sample preparation for SEM involved the sprinkling of the powder sample on a double-sided carbon tape mounted on the SEM stub. Images were taken with a 5 kV accelerating voltage using a triple detector system.

The infrared spectra were acquired at room temperature with a Nicolet 380 ATR-FTIR spectrometer (Thermo Scientific, USA). Sixteen scans were averaged for each sample in the range of 4000–400 cm⁻¹.

The X-ray diffraction (XRD) patterns of the catalyst were recorded by an Empyrean PANalytical X-ray diffractometer using Cu K (λ = 0.154 nm) as the radiation source in the 2θ range 10–80° with a step size of 0.026.

RESULTS AND DISCUSSION

Characteristics of the catalyst

The analysis of nitrogen adsorption-desorption allows determining parameters of the carbon catalyst’s porous structure: specific surface area, total pore volume, and micropores. The tested catalyst has surface area values of 452 m²/g and a total pore volume of 0.496 cm³/g. The micropore volume estimated based on N2 adsorption was 0.139 cm³/g. Fe content in the tested material was at the level of 26.67%. The above results show that it was possible to obtain a carbon catalyst with a relatively high specific surface area with simultaneous high metal content in the catalyst.

Figure 2 shows the adsorption-desorption isotherm for the Fe/O_AC catalyst. In the UPAC classification, the isotherm corresponds to Type-II. Except for the pressure range p/p0 =0.2–0.8, in which it is approximately parallel to the x-axis, which makes it similar in this pressure range to the Type-I isotherm and proves a very small share of mesopores. The isotherm in this section is similar to the Type-I isotherm. Very weak adsorption can be seen here, up to the relative pressure p/p0 of 0.8. With such high pressures, the macropores are filled. Quantachrome Instruments is not used to measure macropores, but it can be concluded that the pore diameter corresponding to p/p0 ≥ 1 is 784 nm. The visible hysteresis loop is defined as the H3 type, which suggests that there are slotted pores.

Figure 2. N2 adsorption-desorption isotherm at −196°C for the obtained Fe/O_AC catalyst

Figure 3 shows the pore size distribution (PSD) of the Fe/O_AC catalyst, determined by the DFT method based on N2 adsorption at −196°C. Based on Fig. 3, the presence of micropores and the absence of mesopores can be found, which is consistent with the conclusions drawn based on Fig. 2. The DFT method allows the calculation of the pore size up to 100 nm. Taking into account that the maximum pore diameter determined by this method is 784 nm, it can be concluded that only macropores larger than 100 nm are present in the sample. Based on Fig. 2, Fig. 3, and the values of textural parameters, it can be concluded that macropores dominate in the sample. There are also micropores and the proportion of mesopores is negligible. It is also possible to estimate the macropore volume up to a diameter of 784 nm by subtracting Vmes from Vtot. Approximate macropore volume up to 784 nm is 0.357 cm³/g.

According to JCPDS card 88-0315 (cubic, Fd-3m) and 79-0416 (cubic, F-43m), the XRD plot showed characteristic peaks of magnetite. Characteristic diffraction peaks of magnetite can be observed at 2θ of 18.32°, 21.26°, 30.32°, 35.65°, 43.30°, 53.87°, 57.33°, 62.87°, 71.50°,
Based on the location and the shape (bordering and intensity) of the peaks, the two first brother signals were identified as magnetite JCPDS card 79-0416. The rest of the signals were assigned to magnetite JCPDS card 88-0315. As all the observed peaks were assigned to the magnetite phase, no peaks for the potential hematite phase could be seen.

The SEM micrographs of Fe/O-AC are shown in Figure 5. SEM images give an idea about the structure and shape of the material. Activated carbon has a smooth, platted structure with slits (Fig. 5a). At magnification equal to 400 000 Fe$_3$O$_4$, nanoparticles on the activated carbon surface were seen. The size of the nanoparticles was about 10–20 nm.

The detailed morphology and structure of the nanoparticles were further investigated by TEM (Fig. 7). The Fe$_3$O$_4$ nanoparticles had a semispherical shape with an average size of 18 nm.

Figure 6 shows the EDX spectrum of Fe/O_AC. The sample contained only carbon and iron. The origin of a very small and bright signal about 1.5 keV is aluminum stubs.

The FTIR spectrum of Fe/O_AC catalyst is shown in Figure 8. The characteristic band at 1628 cm$^{-1}$ and wide band between 3000 and 3750 cm$^{-1}$ is attributed to the adsorbed water’s existence. In specific, the broad bands (3000–3750 cm$^{-1}$) can be assigned to OH– stretching vibration mode of adsorbed water and the bending vibration of H$_2$O is observed at 1628 cm$^{-1}$. The appearance of two well-defined peaks between 440 and 640 cm$^{-1}$ is due to iron–oxygen (Fe-O), which confirmed that the synthesized nanoparticles are iron oxide.

The alpha-pinene autoxidation

In the first stage of research on the Fe/O_AC catalyst activity, the influence of temperature on the course of alpha-pinene autoxidation was checked. The reaction parameters were as follows: temperature in the range of 70–120°C, amount of catalyst 1 wt.%, in relation to alpha-pinene, reaction time 2 and 24 hours. Figure 9
and Figure 10 show the effect of temperature on alpha-pinenone autoxidation. The highest conversion of alpha-pinene (37.5 mol%) was obtained after 24h at 90°C. Above, and below this temperature, the alpha-pinene conversion is lower. The selectivity of alpha-pinene oxide decreases with the progress of the reaction, from 25–30 mol% after 2 hours to 0–15 mol% after 24 hours. This is due to post-reactions where alpha-pinene oxide reacts to form campholenic aldehyde. As the reaction progresses, the selectivity of verbenol and verbenone also increases. Above 110°C, after 24 hours, a significant decrease in the selectivity of verbenol and the lack of alpha-pinene oxide in the post-reaction mixture can be noticed; it is related to the dimerization and polymerization reactions that take place at higher temperatures. The most preferred reaction temperature is 90°C due to the highest conversion of alpha-pinene in the studied temperature range.

The studies on the effect of the catalyst amount are presented in Figure 11 and Figure 12. The highest alpha-pinene conversion value (37.5 mol%) for the alpha-pinene oxide selectivity (14.9 mol%) was obtained after 24 hours with the catalyst amount of 1 wt.%. For higher catalyst contents in the post-reaction mixture, a significant decrease in the selectivity of alpha-pinene oxide and a decrease in conversion can be noticed. This is due to the very low amount of oxygen in the reaction mixture, resulting in subsequent reactions taking place
ties. The catalyst allowed to obtain the conversion of alpha-pinene oxide, verbenone, verbenol, and campfolenic aldehyde. These compounds are used in the perfumery and cosmetics industry due to their fragrance properties. In the presence of the catalyst in the absence of an adequate amount of oxidant, taking into account the conversion of alpha-pinene and the selectivity of alpha-pinene oxide after 24 hours, the most preferred catalyst content is 1 wt.%.

CONCLUSIONS

The paper presents an ecological method of processing waste such as orange peels into activated carbon and then the use of the material obtained in this way for the synthesis of a Fe-doped carbon catalyst. A relatively high specific surface characterizes the obtained catalyst with a Fe content of 26.67 wt.% and the presence of micropores. The research showed that the obtained Fe/O_AC catalyst was an active catalyst for alpha-pinene autoxidation. The main products of this reaction were: alpha-pinene oxide, verbenone, verbenol, and campfolenic aldehyde. These compounds are used in the perfumery and cosmetics industry due to their fragrance properties. The catalyst allowed to obtain the conversion of alpha-pinene oxide of 14.9 mol% under the most favorable reaction conditions (temperature 90°C, catalyst content in the reaction mixture 1 wt.%, reaction time 24 hours).

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