Hydrogenation of Birch Wood in Supercritical Ethanol with Iridium and Palladium-Iridium Catalysts

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Abstract. Iridium and palladium-iridium catalysts on carbon nanotubes were obtained by the hydrothermal method. The effect of the resulting catalysts on the yield and composition of birch wood hydrogenation products obtained in supercritical ethanol at 250 °C for 3 hours was studied. The influence of iridium and iridium-palladium catalysts in the process of hydrogenation of birch wood on the yield and composition of products has been established. The use of iridium-palladium catalysts in the process of hydrogenation of birch wood leads to an increase in its conversion by 40 wt. %, the yield of liquid products by 8 wt. %, while reducing the yield of solid products by 3 wt. % and gaseous products by 6 wt. %. In the presence of catalysts during the hydrogenation of birch wood, the yield of monomeric methoxyphenols increases to 47 wt. %.

Keywords: hydrogenation, birch, palladium, iridium, carbon nanotubes, reductive catalytic fractionation.

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Гидрирование древесины березы в сверхкритическом этаноле в присутствии иридиевых и палладий-иридиевых катализаторов

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Аннотация. Получены гидротермальным методом иридиевые и палладий-иридиевые катализаторы на углеродных нанотрубках. Изучено их влияние на выход и состав продуктов гидрирования древесины березы, полученных в сверхкритическом этаноле при 250 °C в течение 3 часов. Установлено влияние иридиевых и иридий-палладиевых катализаторов в процессе гидрирования древесины березы на выход и состав продуктов. Использование иридий-палладиевых катализаторов в процессе гидрирования древесины березы приводит к повышению ее конверсии на 40 мас. %, выхода жидких продуктов на 8 мас. %, при одновременном снижении выхода твердых продуктов на 3 мас. % и газообразных продуктов на 6 мас. %. В присутствии катализаторов при гидрировании древесины березы выход мономерных метоксифенолов увеличивается до 47 мас. %.

Ключевые слова: гидрогенизация, береза, палладий, иридий, углеродные нанотрубки, восстановительно-каталитическое фракционирование.

Introduction

The use of lignocellulosic biomass as an alternative to traditional petroleum feedstocks to obtain valuable chemical products from it is a promising strategy for sustainable development [1]. Woody biomass consists of three main components – cellulose, lignin and hemicelluloses, and has a complex structure, which makes it difficult to chemically process it into sought-after chemical compounds [2, 3].

Traditional industrial technologies are focused on processing predominantly the cellulose component of woody biomass [2]. At the same time, lignin, being one of the main components of biomass and a potential source of valuable aromatic substances, remains as a waste [4].

Lignin is an alkyl aromatic heteropolymer commonly found in the cell walls of land plants, where it has many physiological functions in plant structure, water and nutrient transport, and defense against microbiological attack [5].

Hemicelluloses are amorphous branched heteropolymers consisting of C 5 and C 6 monosaccharides and uronic acids. The most common type of hemicellulose in deciduous wood and non-woody plants is xylan [6].

A promising direction aimed at the comprehensive processing of all components of lignocellulosic biomass, without preliminary extraction of lignin, is reductive catalytic fractionation (RCF). The RCF process ensures depolymerization of the lignin component of the biomass, while retaining the bulk of the cellulosic product.

To effectively implement the RCF process, heterogeneous metal catalysts based on platinum group metals (Ru, Pt, Pd), as well as based on Ni, Mo, etc., deposited on stable supports are used. Catalytic hydrogenation of lignins with hydrogen in the presence of solid catalysts Ru/C [7], Pt/C [8], Rh/C [9], ZnPd/C [10], Ni/C [11] is accompanied by an increase in the degree of their depolymerization and an increase in yield monomeric and dimeric phenolic products, compared with non-catalytic thermal dissolution of lignins in aliphatic alcohols.

In a study [12] with a catalyst based on iridium modified with rhenium oxide supported on SiO_2 (Ir-ReOx/SiO_2), a high yield of cyclohexane (up to 100 %) and naphthenes (44.3 %) was achieved during the conversion of model compounds and lignin raw materials. respectively. ReO_x has been shown to be primarily responsible for the cleavage of C-O bonds, while Ir is responsible for hydrodeoxygenation and saturation of benzene rings.

But the high price, limited quantity on Earth, associated with complex isolation and processing, hinder its future use. Thus, it is necessary to develop the immobilization of a homogeneous iridium complex on solid supports without loss of catalytic activity [13].

Since the RCF process is carried out at fairly high temperatures and pressures, the catalysts must be sufficiently stable under hydrothermal conditions and not subject to deactivation. The study [14] reported the first heterogeneous iridium catalyst supported on Nb_2O_5. This catalyst is capable of combining complete conversion during the hydrodeoxygenation of lignin-derived phenols to hydrocarbons with noticeable selectivity for aromatic compounds. Monooxygenated phenols such as 4-phenylphenol, 4-cyclohexylphenol and naphthol were completely converted to deoxygenated hydrocarbons in less than 10 hours, suggesting that the Ir/Nb2O5 combination does provide a synergistic effect to enhance hydrodeoxygenation compared to iridium-based molecular compounds.

In the study [15], with a catalyst based on palladium (0.25 wt. %) supported on CN_x, a high overall monomer yield (52.7 %) and a high degree of delignification (87.1 %) were achieved. This can be explained by more active hydrogenolysis of C–O bonds in native lignin when using this catalyst. The main phenolic monomers obtained were 4-n-propylguaiacol (8.66 %) and 4-n-propylsyringol (28.9 %).

The highest degree of delignification was achieved when using catalysts based on palladium supported on activated carbon, 95.5 % and 98.1 % at 0.25 % and 5 % palladium content, respectively.

The purpose of this work is to establish the influence of iridium and palladium-iridium catalysts on the yield and composition of products of reductive catalytic fractionation of birch wood.

Materials and Methods

Method for obtaining a catalyst

In this work we used: potassium hexachloroiridate(IV) (synthesized according to the method described in [16]); tetraammine palladium(II) chloride (synthesized according to the procedure [17]); hydrochloric acid – "special purity" 20–4"; sodium tetrahydride borate – "reagent grade"; potassium hydroxide – "reagent grade", aqueous ammonia "special purity grade". 23–5"; deionized water prepared using the Direct-Q3 water purification system (Millipore, USA).

The synthesis of catalysts was carried out in titanium autoclaves with fluoroplastic liners at a temperature of 180 °C. Platinum metals were deposited using a hydrothermal method onto a carbon material based on nanotubes (CNTs) [17]. Carbon supports were pre-treated in 0.05 M KOH at 180 °C for 60 minutes.

The procedure for hydrothermal preparation of Ir/C and Ir-Pd/C catalysts is described in detail in [18]. A weighed portion of the carbon carrier (1 g) was placed in the autoclave, and a freshly prepared solution of potassium hexachloroiridate(IV) was added, obtained by dissolving a given weight of salt in deionized water and 10.0 ml of a 1 M solution of potassium hydroxide. A sample of the reducing agent (sodium tetrahydride borate) was placed in a cup placed on the inner surface of the autoclave lid. The autoclave was sealed and heated in an air thermostat in a vertical position for 40 min to 180 °C. After heating, stirring was turned on, ensuring phase mixing. After 15 minutes, the autoclave was cooled with running water and opened. The precipitate, in the form of a black powder, was washed repeatedly with hot distilled water and separated in a CR 4000 centrifuge (Centurion Scientific, UK) for 15 min at 4000 rpm. The material was dried under vacuum conditions at a temperature of 80 °C.

To obtain a bimetallic catalyst, palladium was applied to the previously prepared Ir/C material by decomposing tetraammine palladium (II) chloride in an autoclave [18]. A sample of Ir/C material was placed in a fluoroplastic reactor, a specified amount of tetraammine palladium (II) chloride was added, 20 cm3 of 0.05 M KOH solution was poured in, and the system was sealed. Stirring was carried out for 15 minutes at 25 °C, after which the autoclave was placed in a thermostat heated to 180ºC for 120 minutes with constant stirring. After the experiment, the autoclave was opened, the solid phase was washed repeatedly with hot deionized water and dried at 80 °C under vacuum conditions. The composition of the obtained catalysts is presented in Table 1.

Electron microscopy studies of the catalysts were performed on an S 5500 scanning electron microscope (Hitachi, Japan).

Table 1. Composition of the obtained catalysts

№	Composition, wt. %		
	Support	Ir	Pd
1	Carbon nanotube	5.0	-
2	Carbon nanotube	4.8	4.8

Method of birch wood hydrogenation

The hydrogenation process was carried out in a ChemRe SYStem R-201 autoclave (Korea) with a volume of 300 ml. The reactor was loaded with 60 ml of ethanol, 3.0 g of substrate and 0.3 g of catalyst. Then the autoclave was hermetically sealed and purged with argon to remove air. Hydrogen was supplied, the initial pressure of which was 4 MPa. The reaction was carried out with constant stirring at a speed of 1000 rpm at a temperature of 250 °C for 3 hours. The rate of temperature rise was 10 °C/min, the time to reach the required temperature was 20–25 minutes. The operating pressure in the reactor was 10.0 MPa. After cooling the reaction mixture to room temperature, the gaseous products were collected in a gasometer, their volume was measured, and the composition was determined by gas chromatography. Then the reaction products were quantitatively discharged from the autoclave by washing with ethanol, and the resulting mixture of liquid and solid products was separated by filtration.

The solid was washed with ethanol until the solvent became colorless. The solvent was removed from the liquid product using a rotary evaporator, and the product was brought to constant weight by drying under vacuum (1 mm Hg) at room temperature. The yield of liquid products (α1), the yield of solid product (α2), the total yield of gaseous products (α3) and wood conversion (χd) were determined using formulas 1–4:

$$\alpha_1 = \frac{m_l\ (g)}{m_{in}\ (g)} \times 100\%, \tag{1}$$

$$\alpha_2 = \frac{m_s\ (g) - m_{cat}\ (g)}{m_{in}\ (g)} \times 100\%, \tag{2}$$

$$\alpha_3 = \frac{m_g\ (g)}{m_{in}\ (g)} \times 100\%, \tag{3}$$

$$\chi_{\text{д}} = \frac{m_{in}\ (g) + m_{cat}\ (g) - m_s(g)}{m_{in}\ (g)} \times 100\%, \tag{4}$$

where m_l – mass of liquid products (g), m_{in} – mass of the initial sample (g), m_s – mass of the solid residue (g),, m_{cat} – mass of the catalyst (g), m_g – mass of gaseous products (g).

Study of birch wood hydrogenation products

The composition of gaseous products of birch wood in supercritical ethanol was determined by GC using a Kristall 2000 M chromatograph (Chromatek, Russia) with a thermal conductivity detector. Carrier gas is helium (flow rate 15 ml/min). Detector temperature 170 °C. To analyze CO and CH4, a column with NaX zeolite (3 m × 2 mm) was used in isothermal mode at a temperature of 60 °C. Analysis of CO_2 and hydrocarbon gases was carried out on a column with Porapak Q in the following mode: 1 min – 60 °C and then increasing the temperature to 180 °C at a rate of 10 °C/min.

The solid product of hydrogenation of birch wood was analyzed for the content of hemicelluloses, cellulose and lignin. The content of residual lignin in the solid product was determined using hydrolysis with 72 % sulfuric acid according to the Komarov method [19], and the content of hemicellulose was determined by gas chromatography (GC) of the resulting hydrolysates [20]. The content and composition of monosaccharides in hydrolysates were determined by GC using a VARIAN-450 GC gas chromatograph with a flame ionization detector and a VF-624ms capillary column with a length of 30 m and an internal diameter of 0.32 mm. Chromatography conditions: helium carrier gas, injector

temperature 250 °C, initial column temperature 50 °C (5 min), temperature increase to 180 °C at a rate of 10 °C/min, hold. at 180 °C for 37 minutes. Before analysis, the hydrolyzate was derivatized according to the procedure in [21] to obtain trimethylsilyl derivatives. Sorbitol was used as an internal standard. Peaks were identified by the retention time of tautomeric forms of monosaccharides. Cellulose was determined in the solid products of flaxseed hydrogenation using the nitrogen-alcohol method (Kürschner-Hoffer) [19].

Liquid ethanol-soluble products of non-catalytic and catalytic hydrogenation of birch wood were analyzed by GC–MS using an Agilent 7890A chromatograph equipped with an Agilent 7000A Triple Quad selective mass detector, recording the total ion current. Product separation was carried out on an HP-5MS capillary column with temperature programming in the range of 40–250 °C. Identification was carried out using the NIST MS Search 2.0 instrument database. To quantify the yield of monomeric compounds, standard substances such as guaiacol, syringol, 2-methoxy-4-methylphenol, isoeugenol, 4-ethylguaiacol, 4-allyl-2,6-dimethoxyphenol (Sigma-Aldrich), ethyl palmitate (Tokyo Chem. Ind.). Phenanthrene was used as an internal standard.

The elemental composition of wood, liquid and solid products of its transformation was determined using an HCNS-O EAFLAS HTM 1112 analyzer (Thermo Quest).

Results and discussion

Features of the structure and structure of catalysts are discussed in detail in [18]. An electron micrograph of a typical sample of an Ir-Pd/C catalyst with a mass fraction of iridium and palladium of 4.8 %, which was obtained by the sequential reduction of complex salts of platinum metals under hydrothermal conditions, is shown in Fig. 1. The initial nanotubes with a transverse diameter of 30–70 nm are coated with nanosized particles platinum metals are predominantly spherical in shape. Iridium has a particle diameter of 4–8 nm, and palladium, which is more prone to aggregation processes, ranges from 10 to 40 nm.

According to the data presented in Table 2, the use of catalysts leads to a decrease in the yield of gaseous products to 1.8 wt. % and an increase in the yield of liquid product to 58 wt. % when using the Ir/C catalyst. When using this catalyst, a decrease in the yield of the solid product is observed (up to 40 wt. %) compared to the non-catalytic experiment (50 wt. %). The use of a Pd-Ir/C bimetallic catalyst
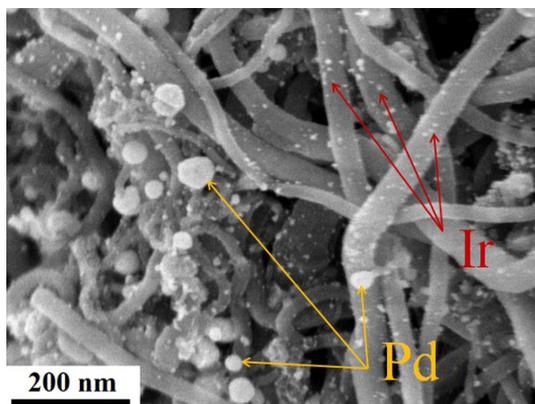
Fig. 1. SEM image of Ir-Pd/C catalyst (4.8 wt. % Ir, 4.8 wt. % Pd)

Table 2. Results of non-catalytic and catalytic hydrogenation of birch wood in supercritical ethanol at 250 °C, 3 hours, P_{H2} = 10.0 MPa

	Conversion, wt. %	Yield liquid products, wt. %	Yield solid products, wt,%	Yield of gas, wt,%			
				CO	CO$_2$	CH$_4$	Sum
w/o catalyst	50.0	42.4	50.0	3.8	3.1	0,7	7,6
Pd-Ir/C	52,5	50,8	47,5	0,3	1,4	0,03	1,73
Ir/C	59,8	58,0	40,2	0,16	1,5	0, 02	1,80

Table 3. Chemical composition of solid products of hydrogenation of birch wood samples in supercritical ethanol at 250 °C, 3 hours, P_{H2} = 10.0 MPa.

sample	Composition, wt. %		
	Hemicellulose	Lignin	Cellulose
w/o catalyst	12.5	17.8	69.7
Pd-Ir/C	3,0	6,8	90,2
Ir/C	4,1	7.6	88,3

leads to a decrease in the yield of gaseous products to 1.7 wt. %, increasing the yield of liquid products to 51 wt. %.

The results of chemical analysis (Table 3) also confirm that the Pd-Ir/C bimetallic catalyst has greater catalytic activity in the process of hydrogenation of birch wood, as evidenced by the yield of lignin in the solid product. When using this catalyst, the lowest lignin content (6.8 wt. %) in the solid product is observed, while the highest cellulose content is observed and amounts to 90 wt. %.

According to the data presented in Fig. 2, during the hydrogenation of birch wood in the case of a catalytic and non-catalytic process, a high conversion of hemicelluloses (more than 96 wt. %) is observed, which is due to the low thermal stability of xylan [22]. The use of an iridium catalyst increases lignin conversion by 30 wt. %, while the use of a palladium-iridium catalyst increases lignin conversion by 40 wt. % compared to the non-catalytic experiment. It should be noted that the use of
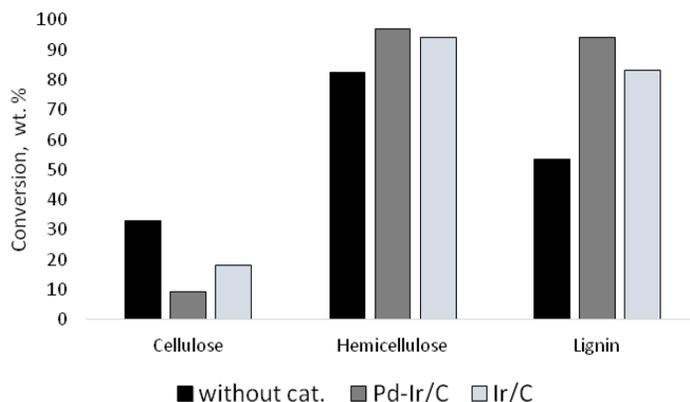
Fig. 2. Conversion of structural components of birch wood during hydrogenation in supercritical ethanol at 250 °C
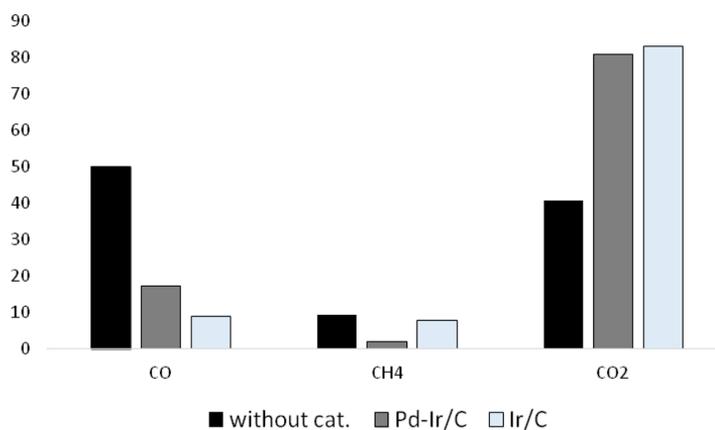
Fig. 3. Composition of gaseous products of hydrogenation of birch wood in supercritical ethanol at 250 °C, 3 hours, $P_{H2} = 10.0$ MPa

catalysts leads to a decrease in cellulose conversion by 15 and 24 wt. % for the iridium and palladium-iridium catalysts, respectively.

According to the data shown in Fig. 3, the composition of the gaseous products of hydrogenation of birch wood consists mainly of carbon monoxide and carbon dioxide and methane. The use of catalysts leads to a change in the ratio between the main components of gaseous products. Thus, the use of iridium and palladium-iridium catalysts leads to a decrease in the content of carbon monoxide and an increase in methane in the gaseous products of hydrogenation of birch wood.

The results of elemental analysis of the composition of the original birch wood and its hydrogenation products are shown in Table 4. Liquid products of catalytic hydrogenation of birch wood contain less oxygen and more hydrogen compared to liquid products of non-catalytic hydrogenation. All this indicates the occurrence of the process of catalytic hydrodeoxygenation of lignin leading to the formation of monomeric and dimeric products from lignin [23–25]. The presence of a catalyst in the reaction medium intensifies the processes of hydrodeoxygenation, which is also indicated by an increase in the yield of carbon dioxide in gaseous products.

The use of iridium and iridium-palladium catalysts in the process of hydrogenation of birch wood in supercritical ethanol leads to an increase in the yield of monomeric methoxyphenols (Table 5). When hydrogenating birch wood, the main monophenolic components are 4-propylsyringol and 4-propanolsyringol. During hydrogenation in the absence of a catalyst, 4-propenylsyringol (0.8

Table 4. Elemental composition of liquid products of hydrogenation of birch wood samples in supercritical ethanol at 250 °C, 3 hours, $P_{H2} = 10.0$ MPa

Sample	C, мас. %	H, мас. %	O, мас. %
Initial birch wood	49,8	6,1	44,1
w/o catalyst	58,6	7,5	33,9
Pd-Ir/C	60,3	8,0	31,7
Ir/C	59,2	7,8	33,0

Table 5. Yield of monomer compounds in liquid products of hydrogenation of birch wood in supercritical ethanol at 250 °C, 3 hours, P_{H2} = 10.0 MPa

Compound	Yield, wt. %*		
	w/o cat.	Ir/C	Pd-Ir/C
4-propenylguaiacol	0.3	0.1	0.1
4-propenylsyringol	0,8	0.2	2.3
4-propylguaiacol	-	0.4	1.0
4-propylsyringol	0.2	5.4	5.3
4-methylsyringol	-	0.4	0.3
4-ethylsyringol	0.1	0.9	0,5
4-propanolsyringol	0.2	2.0	30.8
Other methoxyphenols	0.1	5.1	7.5
Total	1.7	14,5	47.8

* – Per mass of Klason lignin

wt. %) predominates. The use of catalysts leads to saturation of the double bond of 4-propenylsyringol, which leads to an increase in the yield of 4-propylsyringol (up to 5.5 wt. %). In addition, the use of catalysts promotes the cleavage of reactive β-O-4 and C–C bonds, which leads to an overall increase in the yields of monophenolic components [26]. The use of a Pd-Ir/C catalyst leads to the production of 4-propanolsyringol in high yield (up to 30 wt. %).

The maximum yield of monomeric methoxyphenols (up to 47.8 wt. %) is observed when using a palladium-iridium catalyst. It is known that bimetallic systems have greater catalytic activity due to the synergistic effect [9]. For example, the Pd/Zn/C bimetallic catalyst demonstrated high efficiency in the depolymerization of native poplar wood lignin in methanol and promoted the formation of 4-propylguaiacol and 4-propylsyringol as the main products, providing a total monomer yield of 54 wt. % [9].

Conclusion

The influence of Ir and – Pd-Ir catalysts deposited on taunite on the yield and composition of birch wood hydrogenation products was studied. It has been shown that the Pd-Ir-taunite bimetallic catalyst has greater activity compared to the monometallic catalyst.

Using a bimetallic catalyst, the yield of monomeric methcosiphenols from lignin reaches 47.8 wt. %, with the main monomer being 4-propanolsyringol with a yield of up to 30 wt. %.

It has been shown that when using the Ir/C catalyst, a decrease in the yield of the solid product is observed (up to 40 wt. %) compared to the non-catalytic experiment (50 wt. %). The use of a Pd-Ir/C bimetallic catalyst leads to a decrease in the yield of gaseous products to 1.7 wt. %, increasing the yield of liquid products to 51 wt. %.

The use of the Ir/C catalyst increases lignin conversion by 30 wt. %, while the use of the Pd-Ir/C catalyst increases lignin conversion by 40 wt. % compared to the non-catalytic experiment.

Conflict of interest

The authors of this work declare that they have no conflict of interest.

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