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## Reductive Catalytic Fractionation of Birch Wood in Ethanol Medium over a Novel Bifunctional Catalyst Ni/HfO<sub>2</sub>

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**Abstract.** A novel bifunctional catalyst based on Ni supported on hafnium oxide was prepared to depolymerise birch wood lignin. A native lignin fraction of birch wood was promptly depolymerised into valuable phenolic monomers, enriched with propenylsyringol through one-pot catalytic reductive fractionation at 225 °C, and 4 MPa H<sub>2</sub> during 3 hours. The yield of liquid products increased from 23 to 37 wt.% under the hydrogenation in the presence of catalyst. Detailed Brunauer-Emmett-Teller, pH of the point of zero charge, and X-ray photoelectron spectroscopy investigations revealed that the metal–acid synergistic effect in the presence of acid sites and of both Ni<sup>2+</sup> and Ni<sup>0</sup> were responsible for the breaking of C–C bond, ester and ether linkages bonds in lignin. Moreover, modifying catalyst by phosphoric acid generated propenylsyringol in higher yield. Overall, this report highlighted the potential of the simple preparation strategy of the bifunctional catalyst based on Ni supported on acidic HfO<sub>2</sub> to depolymerize wood lignin and proposed possible mechanism for reductive catalytic fractionation of birch wood biomass.

**Keywords:** birch wood, hafnium, fractionation, hydrogenation.

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## Восстановительное каталитическое фракционирование древесины березы в среде этанола с использованием нового бифункционального катализатора Ni/HfO<sub>2</sub>

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**Аннотация.** Новый бифункциональный катализатор на основе Ni, нанесенного на оксид гафния, был использован для деполимеризации лигнина древесины березы. Фракция нативного лигнина древесины березы быстро деполимеризовалась в ценные фенольные мономеры, обогащенные пропенилсиринголом посредством one-pot каталитического восстановительного фракционирования при 225 °С и 4 МПа H<sub>2</sub> в течение 3 часов. При гидрировании в присутствии катализатора выход жидких продуктов увеличился с 23 до 37 мас.%. Подробные исследования методами Брунауэра-Эммета-Теллера, рН точки нулевого заряда и рентгеновской фотоэлектронной спектроскопии показали, что синергетический эффект в присутствии кислотных и металлических центров, таких как Ni<sup>2+</sup> и Ni<sup>0</sup>, способствовал разрыву C–C связей, сложноэфирных и эфирных связей в лигнине. Более того, модификация катализатора фосфорной кислотой способствовала генерированию пропенилсирингола с более высоким выходом. В целом эти исследования демонстрируют потенциал простого метода приготовления бифункционального катализатора на основе Ni, нанесенного на кислотный HfO<sub>2</sub>, для деполимеризации древесного лигнина и предлагают возможный механизм восстановительного каталитического фракционирования биомассы древесины березы.

**Ключевые слова:** древесина березы, гафний, фракционирование, гидрирование.

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## 1. Introduction

In recent years, there are a sharp increase in interest to develop of new catalytic processes for the converting lignocellulosic biomass to biochemicals and biofuels. In particular, lignin, which makes up approximately 30 wt% of all nonfossil organic carbon and near 20–35 wt% of dry wood, is a promising biomass resource [1–3].

Recent research on the mechanism of lignocellulose catalytic hydrogenation has mainly focused on the reaction pathways and the correlations between the catalyst structure and the hydrogenation performance of model compounds [4, 5]. The model compounds contains both phenolic hydroxyl groups ( $C_{\text{aryl}}\text{-OH}$ ) and ether bonds ( $C_{\text{aryl}}\text{-OCH}_3$ ), and their catalytic hydrogenation gives the lignin-derived phenols such as guaiacol and eugenol [6].

Hardwood, which is a common feedstock used for reductive catalytic fractionation [7], contains approximately 18–25 wt% of lignin mainly comprising S and G units. Because S units lack a free ortho-position, the hardwood lignin cannot form 5–5 and  $\beta$ -5 interunit bonds by radical coupling during delignification [8, 9]. The breakage of the  $\beta$ -O-4 and  $\alpha$ -O-4 bonds was observed during the depolymerization reactions of the lignin [10].

The main trend for lignocellulose hydrogenation catalysts is the use of transition metals supported on various supports [11, 12]. Considering the expense of precious metal catalysts, the cheaper non-precious metal catalysts have become more promising in hydrodeoxygenation reactions [13, 14].

In the literature, there are some examples of the use of solid catalysts based on noble and non-noble metals supported on mesoporous oxide carries in the reductive catalytic fractionation of lignocellulose biomass [15, 16]. Zirconium oxide was used as a support for the reductive catalytic fractionation of lignocellulose [16]. The monoclinic  $\text{ZrO}_2$  provides more acidic sites (Lewis type) due to the higher  $\text{Zr}^{4+}$  density compared to tetragonal  $\text{ZrO}_2$  [17]. The acidity of the zirconium carrier has a certain contribution to catalytic activity, but the bifunctional metal-containing catalysts are more active in the reductive fractionation due to synergy effect of metallic and acidic sites [18].

Catalytic hydrogenolysis of lignocellulose biomass needs rather severe reaction conditions and energy consumption. Thus, it is necessary to explore efficient and more stable catalysts for the lignocellulose hydrogenolysis.

Hafnium oxide ( $\text{HfO}_2$ ) – a refractory material, has high temperature resistance and good stability [19]. Hafnium oxide has properties similar to zirconia. In recent years, many researchers have used hafnium-based catalysts in catalytic conversions of biomass platform molecules [20–22]. There are also a few reports where the hafnium materials are applied for the reductive catalytic fractionation of lignocellulose or for the hydrogenolysis of biomass derivatives [23, 24]. It is a good choice to use the hafnium oxide as a support material in the preparation of bifunctional catalysts for the lignocellulose hydrogenolysis. Also nickel-containing bifunctional catalysts have been in lignin hydrogenolysis reaction [25, 26].

In this research the novel bifunctional catalyst based on Ni supported on hafnium oxide was prepared and characterized. The properties of this catalyst was studied in the process of reductive fractionation of birch wood biomass.

## 2. Materials and Methods

### 2.1. Preparation of Ni/HfO<sub>2</sub> catalysts

The Ni/HfO<sub>2</sub> catalysts were prepared using the incipient-wetness impregnation method. HfO<sub>2</sub> was impregnated with a NiCl<sub>2</sub>·6H<sub>2</sub>O solution with continuous stirring at room temperature for 30 min. Then the sample was kept wet overnight at room temperature, and then dried at 60 °C for 4 h in an electric blast drying oven. Finally the catalyst was reduced at 450 °C for 2 h in a flow of hydrogen (heating rate 3.7 °C/min). After cooling the catalyst was passivated in the flow of a mixture of O<sub>2</sub> (2 %) and nitrogen. The catalysts of the composition x-Ni/HfO<sub>2</sub> (x=1, 5, 10 wt%) were prepared.

### 2.2. Preparation of supports HfO<sub>2</sub>-S and HfO<sub>2</sub>-P

The HfO<sub>2</sub> was pretreated using 2 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution. The solution was dried at 120 °C and calcined at 400 °C for 4 h in Muffle furnace to obtain support HfO<sub>2</sub>-P. The HfO<sub>2</sub> was treated by sulfuric acid (2 M H<sub>2</sub>SO<sub>4</sub>) solution, the sample was dried at 200 °C and calcined at 650 °C for 4 h in Muffle furnace to obtain support HfO<sub>2</sub>-S.

### 2.3. Preparation of Ni/HfO<sub>2</sub>-S and Ni/HfO<sub>2</sub>-P catalysts

The Ni/HfO<sub>2</sub>-P catalyst was prepared by the incipient-wetness impregnation method. HfO<sub>2</sub>-P was impregnated with a NiCl<sub>2</sub>·6H<sub>2</sub>O solution containing with continuous stirring at room temperature for 30 min. Then the solid was aged at room temperature for 12 h, and dried at 120 °C for 5 h in an electric blast drying oven. Subsequently, the solid was ground into fine powder and reduced for 2 h in an H<sub>2</sub> flow at 450 °C (heating rate 3.7 °C/min). Then the solid was passivated in a flow of a mixture of O<sub>2</sub> (2 %) and N<sub>2</sub> to get the final Ni/HfO<sub>2</sub>-P catalyst. The loading of Ni was 5 % mas.

Catalyst Ni/HfO<sub>2</sub>-S with the same loading of Ni was prepared following the same procedure but just using the HfO<sub>2</sub>-S as the support.

### 2.4. Reductive Catalytic Fractionation

Reductive catalytic fractionation was carried out in a 300 mL autoclave reactor equipped with a magnetic drive stirrer in an ethanol medium in the presence of bifunctional catalysts. A mixture of 3.0 g of initial birch wood, 0.3 g of HfO<sub>2</sub>-supported metal Ni catalysts, and 60 mL of ethanol solution was placed in the reactor. After sealing the reactor, a leak test was performed with argon. Thereafter, the reactor was flushed with argon to remove air and pressurized with H<sub>2</sub> to 4 MPa at room temperature.

The reactants were stirred at 1000 rpm and heated to 225 °C with a heating rate of 10 °C/min. The pressure of 4 MPa was reached at a temperature of 225 °C. The duration of heat treatment at the final temperature was 3 h before the mixture was cooled rapidly to room temperature. The reaction mixture was further depressurized to atmospheric pressure, and the liquid and solid products were collected.

The residual solids (mixture of remaining biomass and the catalyst) were separated from the liquid through filtration and rinse with ethanol, exposed to ambient air.

Ethanol was removed from the product solution using a rotary evaporator and the residue was brought to constant weight in vacuum (1 mmHg) at room temperature. The liquid yield Y<sub>L</sub> (wt.%) was calculated as follows:

$$Y_L = \frac{m_L}{m_B} \times 100\%$$

where  $m_L$  is the liquid products (g) mass,  $m_B$  is the birch wood mass (g). The solid residue yield  $Y_{SR}$  (wt.%) was calculated as follows:

$$Y_{SR} = \frac{m_{SR} - m_{cat}}{m_B} \times 100\%$$

where  $m_{SR}$  is the solid residue (g) mass after extraction,  $m_{cat}$  is the catalyst (g) mass. The yield of the gaseous product  $Y_G$  (wt.%) was calculated as follows:

$$Y_G = \frac{m_G}{m_B} \times 100\%$$

where  $m_G$  is the gaseous product (g) mass.

### 2.5. Methods of catalysts characterization and products

Specific surface area and pore volume of the catalysts were determined by equilibrium nitrogen adsorption at 77 K using an analyzer of specific surface area and porosity Micromeritics ASAP 2020.

The surface morphology was studied using a Hitachi TM4000 Plus scanning electron microscope with an attachment for energy-dispersive microanalysis for a qualitative and quantitative X-ray spectral microanalysis of the samples' composition.

The acidity of the catalysts was evaluated by the point of zero charge (PZC) according to the Sorenson–de Bruyn method [27]. A total of 10 mL of distilled water was placed in a potentiometric cell, then successively in small portions (0.01 g); the conditions were not accurately characterized, and the stoichiometry was added to the test sample with continuous stirring with a magnetic stirrer at time intervals of 5–10 min until a constant potential of the glass electrode was reached [27].

GC–MS analysis of liquid products was carried out using an Agilent 7890 A chromatograph equipped with an Agilent 7000 A Triple Quad mass selective detector (Agilent, Santa Clara, CA, USA, 2008) (with an HP-5MS capillary column (30 m × 0.25 mm inner diameter)), by recording the total ion current. The chromatographic separation of ethanol soluble products was performed by increasing the temperature from 40 to 200 °C at a rate of 3 °C/min.

A VARIAN-450 GC gas chromatograph (Varian Inc., Palo Alto, CA, USA), a flame ionization detector, a VF-624 ms capillary column of 30 m length and 0.32 mm inner diameter with helium as the gas carrier at the injector temperature of 250 °C were used for the analysis of saccharides. Before the analysis, the solution was derivatized according to the procedure described elsewhere [28] to produce trimethylsilyl derivatives. Sorbitol was used as an internal standard. The peaks were identified using the retention times of tautomeric forms of monosaccharides.

The solid products of birch wood thermal transformation were analyzed for the contents of hemicelluloses, cellulose and lignin. The lignin content was determined by the Kovarov method [28] by hydrolyzing the solid product with 72 % sulfuric acid. The content of hemicelluloses was determined by hydrolyzing the solid product with 2 % sulfuric acid.

## 3. Results and discussion

The catalyst Ni/HfO<sub>2</sub> were prepared simply by incipient- wetness impregnation method. This is the first report on the preparation of nickel catalyst using hafnium oxide as the support for the reductive catalytic fractionation of birch wood in ethanol medium. Fig. 1 demonstrates the scheme of Ni/HfO<sub>2</sub> catalyst preparation and its application in birch wood hydrogenation.

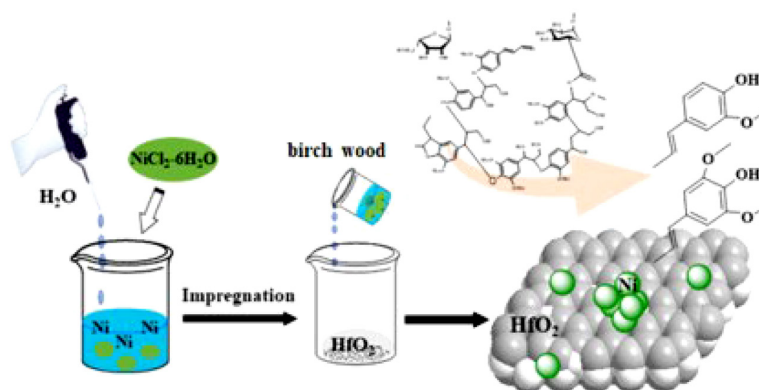


Fig. 1. Scheme of the Ni/HfO<sub>2</sub> catalyst preparation and its application in the reductive catalytic fractionation of birch wood into phenolic compounds

### 3.1. Characterization of the Catalysts

The characteristics of the catalyst were studied by BET and XPS methods. According to BET data the 5 % Ni/HfO<sub>2</sub> catalyst has the lowest surface area. The average pore size and the pH of the point of zero charge (pH<sub>PZC</sub>) are reduced as the nickel content increases in the catalyst. The increase in Ni content causes the pore channel to be clogged and the pore size to be reduced. The pH<sub>PZC</sub> of HfO<sub>2</sub> is 3.12 and the pH<sub>PZC</sub> value increases in the catalysts' series 1 % Ni/HfO<sub>2</sub>, 5 % Ni/HfO<sub>2</sub> and 10 % Ni/HfO<sub>2</sub> from 7.78 up to 8.29. The catalyst modified with sulfuric acid has the largest surface area (45 m<sup>2</sup>/g), and the catalyst modified with phosphoric acid has the highest acidity (3.69 of pH<sub>PZC</sub>). The number of acid sites is dependent on the presence of metals due to the interaction between Ni ions and HfO<sub>2</sub> support.

Method of XPS spectroscopy was used to analyze the valence state of Ni in the reduced and passivated Ni/HfO<sub>2</sub> catalyst. The main Ni 2p<sub>3/2</sub> signal was composed of two contributions at 855.8 and 858.7 eV, where the former was as-signed to Ni<sup>2+</sup> and the latter to Ni<sup>3+</sup>. The higher bonding energy in Ni/HfO<sub>2</sub> could be caused by electron transfer from Ni atoms and suggests that the electronic structure of the Ni species is modified by HfO<sub>2</sub> support [5]. The appearance of satellite peaks between 874 and 885 eV also confirmed the existence of Ni<sup>2+</sup> (Ni 2p<sub>1/2</sub> signal). They showed two unique Ni species that

Table 1. Some characteristics of the Ni/HfO<sub>2</sub> catalysts

Sample	S <sub>BET</sub> (m <sup>2</sup> /g) <sup>a</sup>	V <sub>pore</sub> Σ (cm <sup>3</sup> /g) <sup>b</sup>	D <sub>pore</sub> (nm) <sup>c</sup>	pH <sub>pzc</sub> <sup>d</sup>
1 % Ni/HfO <sub>2</sub>	12	0.07	23.3	7.78
5 % Ni/HfO <sub>2</sub>	9	0.05	22.8	7.97
10 % Ni/HfO <sub>2</sub>	10	0.06	21.0	8.29
5 % Ni/HfO <sub>2</sub> -S	45	0.09	8.1	6.94
5 % Ni/HfO <sub>2</sub> -P	2	0.01	20.2	3.69
HfO <sub>2</sub>	12	0.07	22.9	3.12

<sup>a</sup> S<sub>BET</sub>: Brunauer-Emmett-Teller (BET) specific surface area.

<sup>b</sup> Volume of pores.

<sup>c</sup> D: average pore size.

<sup>d</sup> pH<sub>PZC</sub> is the pH of the point of zero charge.

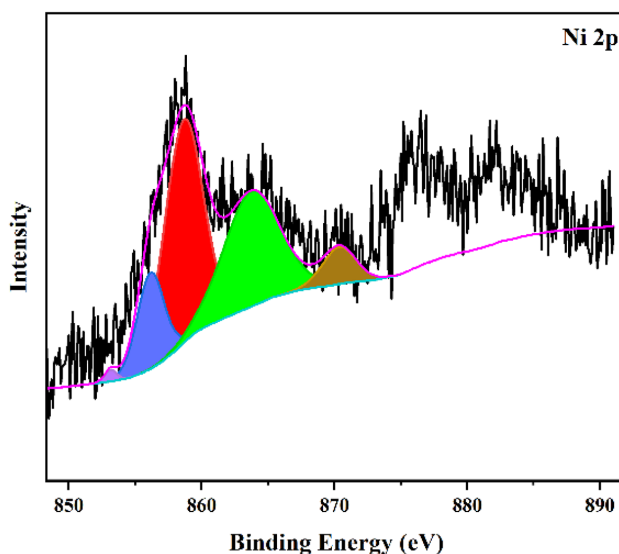


Fig. 2. X-ray photoelectron spectroscopy spectrum Ni 2p (5 % Ni/HfO<sub>2</sub>)

all correspond to metallic Ni (853.0 and 870.1 eV). Therefore, the prepared Ni-HfO<sub>2</sub> catalyst contains both Ni<sup>2+/3+</sup> and Ni<sup>0</sup> species.

### 3.2. Yield of products of birch wood reductive fractionation

The process of birch wood hydrogenation was studied at 225 °C in ethanol medium in the presence of different HfO<sub>2</sub>-supported nickel catalysts. The data on the yields of liquid, solid and gaseous products of wood hydrogenation are given in the Table 2. All catalysts increase the yield of liquid products (from 23 to 37 wt%) and reduce in the yield of solid products (from 53 to 38 wt%) compared to non-catalytic hydrogenation of the birch wood. The yield of gases products was practically the same in catalytic and non-catalytic processes. But the acid-modified catalyst 5 % Ni/HfO<sub>2</sub>-S reduced the formation of gaseous products.

### 3.3. Composition of liquid products of birch wood reductive fractionation

According to GC-MS data the alkyl derivatives of syringyl-type methoxyphenols predominate in the liquid products of birch wood hydrogenation (Table 3). A total yield of monomer alkyl derivatives of methoxyphenols in the liquid products of the non-catalytic hydrogenation process is 4.9 wt%. In the presence of catalysts 1 % Ni/HfO<sub>2</sub>, 5 % Ni/HfO<sub>2</sub>, 10 % Ni/HfO<sub>2</sub>, 5 % Ni/HfO<sub>2</sub>-S and 5 % Ni/HfO<sub>2</sub>-P the total yield of methoxyphenols derivatives increases to 10.3, 10.6, 8.6, 7.0 and 10.0 wt% accordingly. The largest increase of the total yield of methoxyphenols was observed for a catalyst containing 5 % Ni on hafnium oxide. But when the content of nickel in the catalyst increased to 10 % or acid modification was used the corresponding total yield of methoxyphenols was decreased. The reduced activity of 10 % Ni/HfO<sub>2</sub> catalyst can be explained by the low content of acidic sites (higher metal and acid sites ratio) [29].

Among the phenolic products of birch hydrogenation the 4-propenylsyringol and 4-propenylguaiacol were detected in most appreciable amounts.

The 4-Propenylsyringol predominates among the monomer compounds formed during non-catalytic wood hydrogenation. In the liquid product of catalytic hydrogenation, the content of monomer compounds are increased by 1.5–2.2 times. The highest content of 4-Propenylsyringol is observed with the Ni/HfO<sub>2</sub>-P catalyst which may be due to its high acidity (pH<sub>pzc</sub> 3.69).

Table 2. Yield of products of birch wood hydrogenation reductive fractionation in ethanol

No	Sample	Yield (wt %)		
		Liquid Products	Solid Products	Gases
1	No Catalyst	23	53	24
2	1 % Ni/HfO <sub>2</sub>	33	40	27
3	5 % Ni/HfO <sub>2</sub>	37	38	25
4	10 % Ni/HfO <sub>2</sub>	37	40	23
5	5 % Ni/HfO <sub>2</sub> -S	29	53	18
6	5 % Ni/HfO <sub>2</sub> -P	35	44	21

Reaction conditions: 3.0 g initial birch wood, 0.3 g catalyst, 60 mL ethanol, 4 MPa H<sub>2</sub>, 225 °C, 3 h.

Table 3. Yields of monomer phenolic compounds in liquid products of birch wood hydrogenation (GS-MS data)

No	Compound	Structure	Yield (wt %)					
			No Catalyst	1 % Ni/HfO <sub>2</sub>	5 % Ni/HfO <sub>2</sub>	10 % Ni/HfO <sub>2</sub>	5 % Ni/HfO <sub>2</sub> -S	5 % Ni/HfO <sub>2</sub> -P
1	4-ethylguaiaicol		0.07	0.10	0.08	-	-	-
2	Syringol		0.11	0.44	0.53	0.30	0.35	0.33
3	4-propylguaiaicol		0.13	0.14	0.13	0.10	0.03	0.07
4	4-propenylguaiaicol		1.50	1.68	1.73	1.53	1.18	1.39
5	4-ethylsyringol		-	0.33	0.30	0.09	0.04	0.19
6	4-propylsyringol		0.33	0.55	0.62	0.43	0.11	0.34
7	4-propenylsyringol		2.60	4.57	4.60	3.77	3.43	5.60
8	Other monomer compounds (wt %)		0.16	2.49	2.61	2.38	1.86	2.08
9	Total yield (wt %)		4.9	10.3	10.6	8.6	7.00	10.00



Modification of the catalyst with sulfuric acid did not result in an increase in monomer yields compared to other catalysts.

Catalysts increase slightly the yield of alkyl derivatives of guaiacol-type methoxyphenols, compared with the non-catalytic hydrogenation process.

Reaction conditions: 3.0 g initial birch wood, 0.3 g catalyst, 60 mL ethanol, 4 MPa H<sub>2</sub>, 225 °C, 3 h.

### 3.4. Composition of solid products of birch wood hydrogenation

All studied catalysts reduce the content of lignin and hemicelluloses in solid products of birch wood hydrogenation and increase the content of cellulose (Table 4). The solid product of wood hydrogenation over the catalyst 1 % Ni/HfO<sub>2</sub> has the highest content of cellulose (77.6 wt%).

Increasing the Ni loading to 5 % in the catalyst results in a slight decrease of the lignin content in the solid residue (from 15.4 to 13.9 wt.%). The higher Ni loading to 10 % results in an increase of the lignin content in solid product. Modification of the catalysts with sulfur and phosphorus acids does not result in significant changes in the lignin and cellulose content in solid products.

### 3.5. Possible mechanism of birch lignin hydrogenation over bifunctional Ni/HfO<sub>2</sub> catalysts

Taking into account the literature data [3, 18], the scheme of the formation of propenyl-enriched methoxyphenols over Ni/HfO<sub>2</sub> catalysts was suggested (Fig. 3).

The breakage of the β-O-4 and α-O-4 bonds was occurred during the lignin depolymerization [10].

Acid and metal sites of catalysts promote the adsorption of reactants and their subsequent hydrogenolysis and hydrogenation.

The deposition of nickel metal on the surface of HfO<sub>2</sub> affects the ratio of the tetragonal/monoclinic form of the support, and increases the ability of the acid sites to crack the C–C bonds [18]. As a result, there is some increase in the yield of syringol.

The acid-catalytic dehydration of propanol derivatives to propenyl derivatives at the acid sites of the catalyst is as the main route of their transformation [26]. Intensification of the 4-propenylsyringol/4-propylsyringol dehydration reaction results in the formation of a small amount of 4-ethylsyringol.

The yield of 4-propylsyringol increases due to the cleavage of α-O-4 bonds which promoted by the of catalyst.

Table 4. Composition of solid products of birch wood hydrogenation

No	Sample	Content (wt %)		
		Cellulose	Hemicelluloses	Lignin
1	Initial birch	47.3	28.5	19.0
2	No Catalyst	69.1	11.0	18.9
3	1 % Ni/HfO <sub>2</sub>	77.6	7.0	15.4
4	5 % Ni/HfO <sub>2</sub>	77.0	9.1	13.9
5	10 % Ni/HfO <sub>2</sub>	73.5	9.8	16.7
6	5 % Ni/HfO <sub>2</sub> -S	72.4	10.7	16.9
7	5 % Ni/HfO <sub>2</sub> -P	76.6	7.3	16.1

Reaction conditions: 3.0 g initial birch wood, 0.3 g catalyst, 60 mL ethanol, 4 MPa H<sub>2</sub>, 225 °C, 3 h.

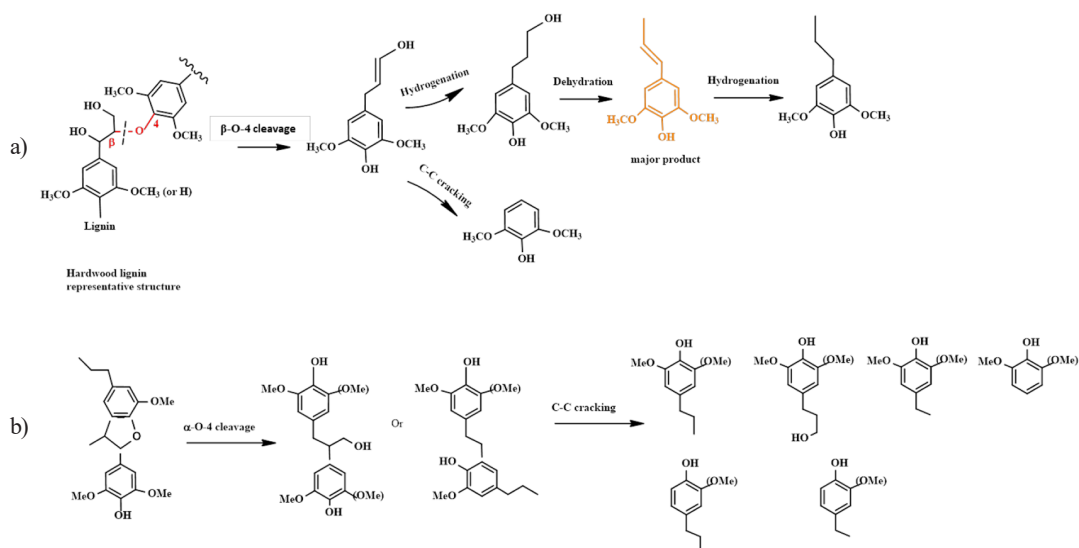


Fig. 3. The scheme of birch lignin hydrogenation over Ni/HfO<sub>2</sub> catalyst: a –  $\beta$ -O-4 bond cleavage, b –  $\alpha$ -O-4 bond cleavage

The 4-propanol-substituted methoxyphenols, along with 4-propyl-substituted methoxyphenols were the main products of the flax shives [26] and abies wood [25] hydrogenation over nickel-containing catalysts.

The data obtained demonstrate the influence of the nature of the catalyst on the composition of phenol compounds formed during lignin hydrogenation. The use of catalysts Ni/carbon results in the predominant formation of propanol-substituted methoxyphenols [25], while catalysts Ni/HfO<sub>2</sub> favor the formation of propenyl-substituted methoxyphenols.

The effective cleavage of the lignin–carbohydrate bonds and the breakage of the  $\beta$ -O-4 and  $\alpha$ -O-4 bonds in the lignin can be attributed to the synergistic effect of the metal and acid sides in the catalyst.

#### 4. Conclusion

Bifunctional catalysts based on Ni supported on HfO<sub>2</sub> was firstly prepared and characterized by physical-chemical methods. The catalysts were active in the reductive depolymerization of native birch wood lignin into valuable aromatics. The depolymerization scope and selectivity of the product were due to the presence of metallic Ni and the acidic nature of the HfO<sub>2</sub> support. The synergetic effect between Ni and acidic sites of HfO<sub>2</sub> benefits the conversion of lignin into high-value liquid aromatic compounds. Catalytic depolymerization of birch lignin in ethanol medium generated liquid products with functionalized aromatic species with yield from 23 up to 37 wt.%.

Catalysts increase the yield of monomers by 2.2 times, compared with the non-catalytic experiment, and the largest increase is observed for a catalyst containing 5 % Ni on hafnium oxide.

The main content is accounted for propenylsyringol. The highest yield (5.6 wt.%) of propenylsyringol is obtained in the presence of a catalyst modified with phosphoric acid (Ni/HfO<sub>2</sub>-P). The analysis of solid hydrogenation products showed that the catalysts decrease the content of lignin in the solid product. At the same time, the catalysts 1 % Ni/HfO<sub>2</sub> and 5 % Ni/HfO<sub>2</sub> increase in the cellulose content up to 77.6 wt.% and 77.0 wt.%. The results obtained showed that in the

presence of a nickel deposited on acidic hafnium oxide, the high selectivity for propenyl-enriched methoxyphenols can be achieved.

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