Highly Effective Schungite-Based Catalyst for Deoxygenation of Biomass Components

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Nowadays, the processes for the conversion of biomass to fuels are of great interest. One of the widely studied reactions is the deoxygenation of oxygen-containing compounds. The process is performed in two main directions: in hydrogen presence (namely hydrodeoxygenation) and using supercritical fluids as a hydrogen source. The modern problem in deoxygenation is catalyst stability and selectivity. Thus, the development of novel catalytic systems is an urgent task. Schungite is a natural carbon-reach material that has high sorption ability and excellent reductive properties. These properties make this material suitable for its use as catalyst support. In this work, the study of the effectiveness of novel schungite-based catalysts in supercritical deoxygenation of fatty acids and bio-oil model compounds is presented. The catalyst synthesis was performed by the recently developed method of Ni hydrothermal deposition on the schungite surface. The synthesized catalysts were tested in the deoxygenation of stearic acid and guayacol in the supercritical hexane. The experimental results showed that the developed catalysts allow 100 % conversion of the substrate to be reached in both processes providing over 90 wt.% of gasoline and diesel-range hydrocarbon yield.

1. Introduction

Production of hydrocarbons from oxygen-containing compounds of biomass is considered to be one of the prospective processes to obtain renewable fuels (biofuel second generation). The second generation of biofuel is typically produced by the hydrodeoxygenation (HDO) process developed by UOP/ENI Ecofining™ (Hongloi et al., 2021). Despite the high productivity, the HDO process consumes a high amount of hydrogen leading to an increase in the process cost. The use of supercritical solvents in biomass conversion seems to be a prospective alternative. Such an approach allows the hydrogen consumption to be significantly decreased. Moreover, deoxygenation in a supercritical state is characterized by the lower duration and the higher catalyst stability because it decreases or prevents the catalyst surface carbonization (Cheah et al., 2021).

The deoxygenation route strongly depends on several factors. First is the gaseous hydrogen presence. In the presence of hydrogen, the main reaction pathway is decarboxylation, while the decarbonylation takes place in an inert atmosphere (Hongloi et al., 2021). The second factor is the catalyst type. It was shown that the use of transition metal catalysts behaviors through the HDO or deoxygenation processes. Noble metals in contrast catalyze decarbonylation/decarboxylation or hydrogenation reactions (Willimann Pimenta et al., 2020).

The catalyst development plays an important role in the deoxygenation process. The catalyst needs to be characterized by the high activity and selectivity to the required products. Also, catalyst stability is an important factor. Some catalysts used in biomass conversion into hydrocarbons tend to be deactivated due to the active phase leaching and surface coking. For this reason, the choice of catalyst support is an urgent task. The materials used as support should have proper porosity and adsorption capacity as well as the Lewis or Bronsted acid sites. Development, characterization and testing of novel catalysts are the main problems to be interested for the studies in bio-based compound deoxygenation.

Schungite is a fullerene-like natural material. It is one of the carbon allotropic modifications. Schungite is a natural carbon-reach material that has high sorption ability and high reductive properties. The main properties of this material are the following: density 2.1 - 2.4 g/cm^3, compressive strength 100 - 200 MPa, electrical

conductivity 1,500 Sm/m, thermal conductivity 3.8 Wt/m, adsorption capacity 20 m^2/g. Such properties make this material suitable for catalyst support. The schungite composition is presented in Table 1 (Mosin and Ignatov, 2013).

Table 1: Schungite composition

	Component												
	C	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	S	H_2O
Content, wt.%	30.0	57.0	0.2	4.0	0.6	1.5	1.2	0.2	0.3	0.2	1.5	1.2	1.7

In the current work, a novel schungite-based catalyst was developed for the conversion of oxygen-containing compounds of biomass into hydrocarbons. Schungite is a cheap material widely used for water purification in Russia. As the catalyst support, schungite tends to be prospective. The aim of the current work is the study of the textural properties, composition, and catalytic activity of the developed schungite-based catalysts. The studied catalytic system can be successfully used in second-generation biofuel production.

2. Materials and methods

2.1 Materials

Schungite powder with particle diameter less than 0.25 mm and humidity of 10 wt.% (Zazhogino field, Karelia Republic, Russian Federation) was used as catalyst support. Nickel acetate ($Ni(CH_3COO)_2 \cdot 4H_2O$, C.P.) was purchased from Aurat (Russian Federation) and used as received as metal precursors. Sodium bicarbonate ($NaHCO_3$, C.P.) was received from Reackim (Russian Federation) and used as a mineralizer. Distilled water was used as a reaction medium for catalyst preparation. Nitrogen (99.9 vol.%, AGA Russia) was used for both catalyst synthesis and deoxygenation procedure.
Stearic acid (99 wt.%) was purchased from Reackim (Russian Federation) and used without purification as a model compound for fatty acid deoxygenation. Guaiacol (C.P.) was received from Acros Organic (USA) and used as a model compound for bio-oil deoxygenation. n-Hexane (C.P.) was purchased from Reackim (Russian Federation) and used as a solvent.

2.2 Catalyst preparation

Schungite powder was preliminarily washed with hexane and acetone to remove the organic contaminants and dried at 70 ± 3 °C. Dry support was sieved and the fraction with the particle size above 150 µm was chosen for catalyst preparation. The deposition of metal was carried out by the precipitation with the superheated water using a high-pressure reactor Parr 4307 (Parr Instrument, USA) at the temperature of 200 °C and the nitrogen pressure of 6.0 MPa for 15 min (Stepacheva et al., 2019). The reaction mixture was filtered after the cooling to room temperature and the synthesized catalysts were dried at 100 ± 5 °C. The resulting catalysts were reduced before the reaction in a glass tube at 300 ± 5 °C with a hydrogen flow (flow rate 30 mL/min) for 3 h.

2.3 Deoxygenation procedure

The deoxygenation experiments were performed in a six-cell Parr Series 5000 Multiple Reactor System (Parr Instrument, USA) with a cell volume of 50 mL (Stepacheva et al., 2020). The stirring of the reaction mixture is carried out using a magnetic stirrer. To estimate the catalyst activity in deoxygenation, 1 g of a model compound, 0.1 g of catalyst, and 30 mL of n-hexane were placed into the reactor cell. The reactor was sealed and purged three times with nitrogen to remove air. Then the nitrogen pressure was set to 3.0 MPa, and the reactor was heated up to 270 °C. The process conditions were chosen according to the critical points of n-hexane (T_c = 234.7 ºC, P_c = 3.03 MPa). After reaching the reaction temperature, the pressure increased up to 9.6 MPa. Experiments were performed with varying process time (from 10 min to 3 h) to maintain phase equilibrium. The reaction mixture stirring was carried out using a magnetic stirrer at 1300 rpm.
The liquid phase was analyzed using gas chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan) equipped with chromatographic column HP-1MS with 30 m length, 0.25 mm diameter, and 0.25 µm film thickness. The column temperature program was set as follows: initial temperature 120 °C was maintained for 5 min then the column was heated up to 250 °C with the rate of 5 °C/min and maintained at 250 °C for 5 min. Helium (volumetric velocity of 20.8 cm^3/s, the pressure of 253.5 kPa) was used as a gas carrier. The injector temperature was 280 °C, the ion source temperature was 260 °C; the interface temperature – 280 °C. For the quantitative estimation, the calibration for pure reactants and main products was carried out.

3. Results and discussion

3.1 Catalyst structure and properties

First, the study of the porous structure for the synthesized schungite-based catalysts was studied by the low-temperature nitrogen physisorption using (Beckman Coulter SA 3100 analyzer (Coulter Corporation, USA). The nitrogen adsorption-desorption isotherms were obtained (Figure 1). The isotherms obtained for the initial schungite, schungite after the treatment in subcritical water, and Ni-containing catalyst have the form of type VI with the hysteresis loop of H4 type. Such isotherms are typical for the mesoporous materials with ink-bottle-type of the pores.

Table 2: Surface area for schungite-based catalyst

Sample	S_{BET}, m^2/g	$S_{Langmuire}$, m^2/g	S_{t-plot}, m^2/g	V_{pore}, cm^3/g
Schungite	22.24	20.96	24.56	0.049
Treated schungite	39.58	36.02	44.90	0.061
10%Ni-Scungite	36.54	33.21	41.31	0.056

When the schungite was treated under the catalyst synthesis conditions, a decrease in the percentage of mesopores with the diameter 20 - 80 nm was observed while the content of pores with a diameter less than 6 nm increased (Figure 2). The surface area of the schungite was found to be increased by almost 2 times after the treatment in subcritical water (Table 2). This can be explained by the leaching of some compounds (i.e. alkali metal oxides, silica, and alumina) from the support. This was confirmed by the elemental analysis (see Table 3).
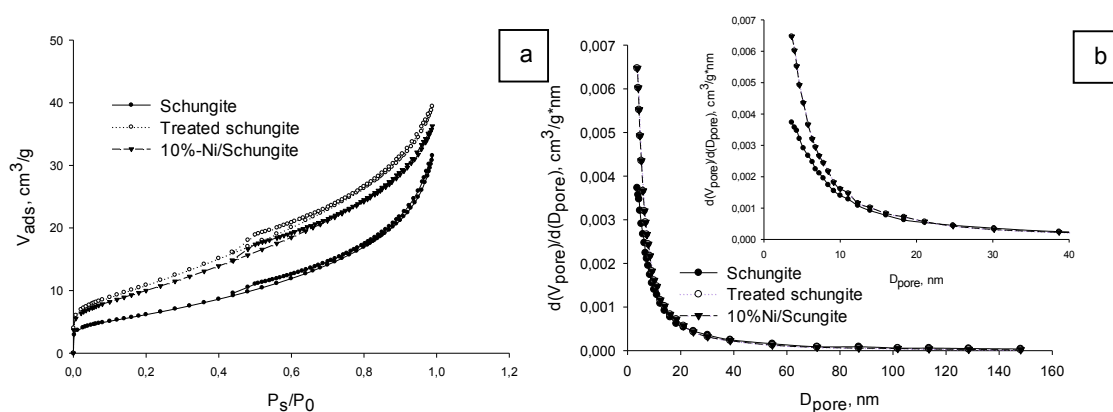

Figure 1: Nitrogen adsorption-desorption isotherms (a) and differential pore size curves (b) for schungite-based catalyst
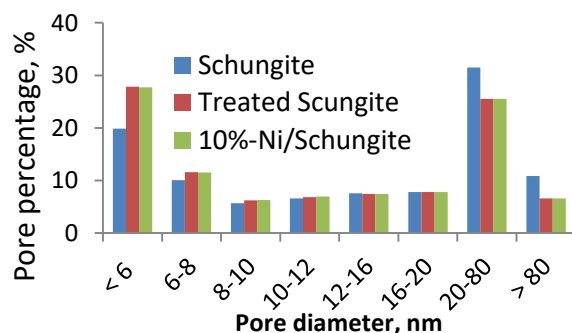

Figure 2: Pore size distribution for schungite-based catalyst

It should be noted that the nickel deposition did not lead to changes in the porous structure in comparison with the treated schungite. This indicates that the metal precursor salt does not affect the catalyst textural properties

and subcritical water plays an important role in the formation of catalyst porosity. In spite, the nickel deposition did not lead to a significant decrease in catalyst surface area, metal concentration in the sample is close to the calculated (see Table 3).

Table 3: Elemental analysis of schungite-based catalyst

Sample	Element concentration, wt. %								
	C	Si	Al	Fe	S	O	K	Mg	Ni
Schungite	31.2	26.6	2.1	1.1	1.2	35.7	1.3	0.8	-
Treated schungite	35.4	25.4	1.9	1.0	1.1	34.4	0.6	0.2	-
10%Ni-Scungite	23.8	24.9	1.9	1.0	1.0	36.8	0.6	0.2	9.8

The study of the catalyst morphology was performed by the TEM analysis using JEOL JEM1010 (JEOL Ltd., Japan) electron microscope. TEM images for the schungite particles and nickel-containing phase are presented in Figure 3. Well seen that the active phase particles are distributed uniformly on the schungite surface. The mean Ni-phase particle diameter was found to be 2.4 nm.
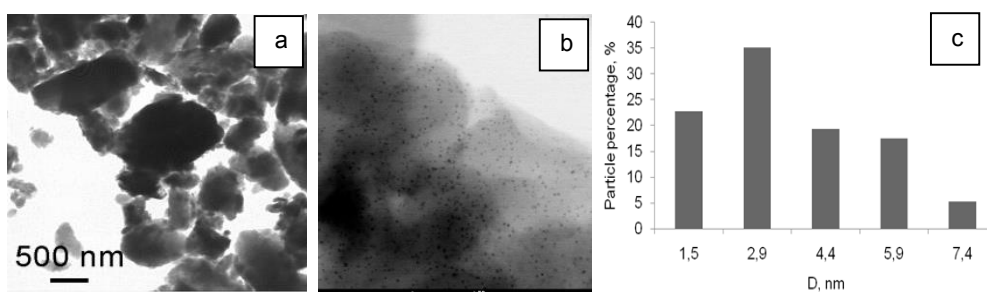

Figure 3: TEM images (a, b) and particle distribution diagram (c) for Ni-containing schungite-based catalyst

To study the nickel state on the catalyst surface, the XPS spectra were recorded using ES-2403 spectrometer equipped with PHOIBOS-100-MCD energy analyzer (Specs GmbH, Germany). Figure 4 presents the high-resolution spectra for Ni 2p sublevel before and after catalyst reduction. The as-synthesized catalyst contains nickel oxyhydroxide with Ni states 2+ and 3+. The partial oxidation of Ni is due to the oxidation activity of subcritical water. After the reduction, the decrease in NiOOH content was observed and the main compound was NiO. Also, some amount of metallic Ni (about 1 wt.%) was formed.
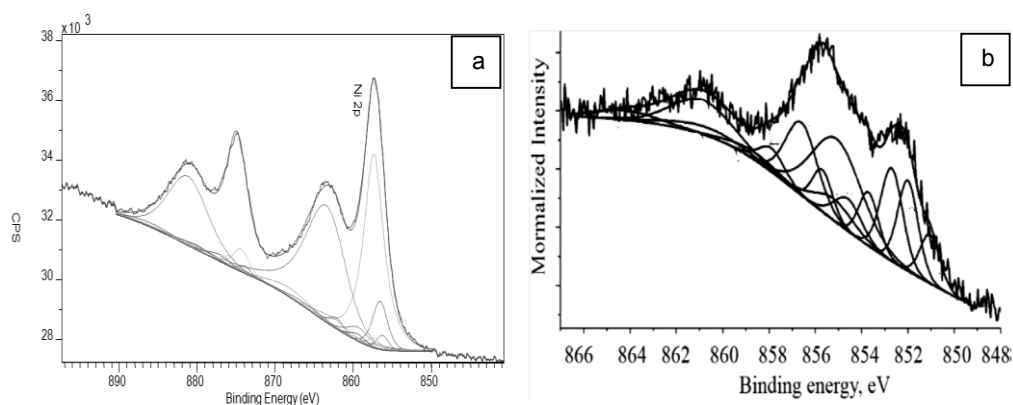

Figure 4: High-resolution XPS spectra for as-synthesized (a) and reduced (b) schungite-based catalyst

3.2 Catalyst activity in deoxygenation

To compare the catalytic activity of the developed scgungite-based catalyst, the Ni-containing samples supported on silica and alumina were synthesized using the same method. The activity in terms of relative rate

and conversion for deoxygenation of stearic acid is presented in Table 4. It is seen that the process relative rate in the presence of 10%-Ni/Schungite is twice higher than that for 10%-Ni/Al_2O_3 and 10%-Ni/SiO_2.

Table 4: Activity of Ni-containing catalysts in stearic acid deoxygenation

	Relative rate, min^{-1}	Stearic acid conversion at 60 min, %
Non-catalytic process	0.034	81.5
10 %-Ni/Al_2O_3	0.041	92.0
10 %-Ni/SiO_2	0.044	92.0
10 %-Ni/Schungite	0.083	95.0

Analyzing the kinetic curves for stearic acid conversion (Figure 5a), it can be seen that the substrate consumption for the process in the presence of silica- and alumina-supported catalysts have an S-type form. This can be explained by the accumulation of adsorbed substrate on the catalyst active sites. In the case of 10 %-Ni/Schungite no decrease in the initial rate was observed due to the high adsorption capacity of schungite. However, at a high conversion degree, a decrease in the deoxygenation rate can be observed. This can be explained by the low rate of product desorption from the catalyst surface. Figure 5b presents the distribution of the stearic acid deoxygenation products. It is seen that schungite-based catalyst provides higher selectivity towards the formation of heptadecane (about 70 wt.%) in comparison with silica- and alumina-based ones. However, some cracking products (C12-C16) were observed. This can be correlated with the lower acidity of schungite and the presence of alkali metals which can play the role of the Ni promoters.
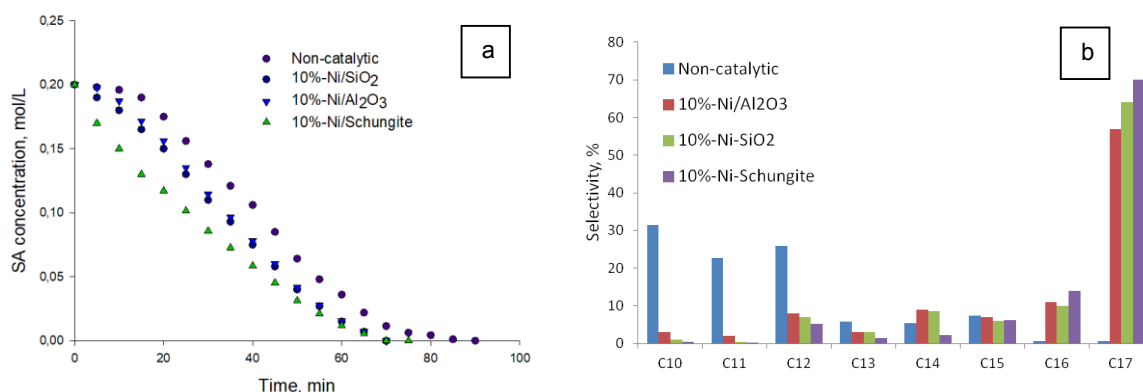

Figure 5: Kinetic curves (a) and product distribution (b) for stearic acid deoxygenation in the presence of Ni-containing catalysts

Table 5: Activity of Ni-containing catalysts in guaiacol deoxygenation

	Relative rate, min^{-1}	Guaiacole conversion at 60 min, %
Non-catalytic process	0.049	78.2
10%-Ni/Al_2O_3	0.065	88.0
10%-Ni/SiO_2	0.067	88.0
10%-Ni/Schungite	0.099	98.1

The activity of the catalysts in the deoxygenation of guaiacol is presented in Table 5. 10 %-Ni/Schungite provides higher activity and guaiacol conversion degree in comparison with 10 %-Ni/Al_2O_3 and 10 %-Ni/SiO_2. The analysis of the kinetic curves for guaiacol conversion (Figure 6a) showed a similar mechanism for all catalysts used. However, 10 %-Ni/Schungite showed a higher rate at the conversion degree from 20 to 70 wt.%. This can be explained by the higher adsorption capacity of schungite. The schungite-based catalyst also provides a higher yield of benzene (up to 90 wt. %) indicating the prevalence of demethoxylation and dehydroxylation reactions in comparison with 10 %-Ni/Al_2O_3 and 10 %-Ni/SiO_2.
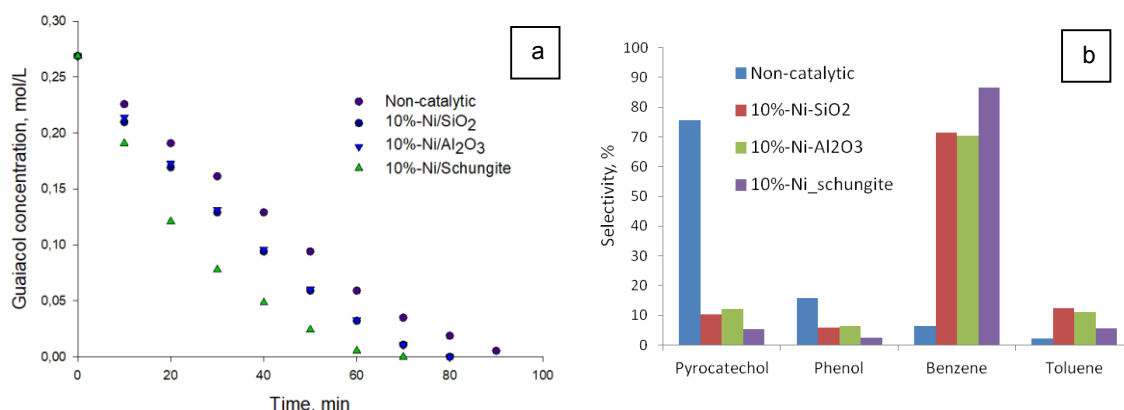
Figure 6: Kinetic curves (a) and product distribution (b) for guaiacol deoxygenation in the presence of Ni-containing catalysts

4. Conclusions

In this work, the schungite-based catalyst for the deoxygenation process was developed. The catalyst synthesis was performed by the hydrothermal deposition of the active phase in subcritical water. When studying the catalyst structure, it was found that the treatment of the initial schungite powder with the subcritical water leads to twice increase in the surface area because of the leaching of some compounds of the mineral (mainly alkali metal oxides). The active phase of the schungite-based catalyst is presented mainly by NiO with a mean particle size of about 2.5 nm.

Testing of the synthesized catalyst in the deoxygenation of model compounds of vegetable oil and bio-oil showed its high activity and selectivity. The 10%-Ni/Schungite catalyst provides over 90 % of oxygen-containing compound conversion for 1 hour of the deoxygenation process. The yield of hydrocarbons in both stearic acid and guaiacol deoxygenation was found to be over 95 %.

Acknowledgments

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