

Deoxygenation of Fatty Acids in Supercritical Hexane over Bimetallic Catalyst for Biodiesel Production

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Deoxygenation process is considered to be a promising way to produce the second generation of biodiesel. The main drawbacks of this process are high temperature, high reaction time and the necessity in hydrogen presence aimed at the formation of saturated diesel-range hydrocarbons. In order to solve the deoxygenation problems, the supercritical fluids can be used as a solvent. The reaction performance in the medium of supercritical fluids allows sufficiently reducing the reaction duration as well as avoiding the use of molecular hydrogen. In the current work, stearic acid deoxygenation in the medium of supercritical hexane in the presence of Ni-Co bimetallic catalyst supported on hypercrosslinked polystyrene by hydrothermal method was studied. The influence of metal loading was estimated. The Ni-Co/HPS catalyst containing 10 wt. % Ni and 10 wt. % Co was found to be an effective catalyst for the deoxygenation process allowing reaching the C₁₆-C₁₈ hydrocarbons yield up to 95 % at 100 % substrate conversion.

1. Introduction

Converting oils and fats into valuable chemicals is one of the promising ways to use renewable sources instead of petroleum. Vegetable oil is a prospective feedstock which can be used for obtaining of fatty acids, fatty acid methyl or ethyl esters, glycerol, fatty alcohols, and aldehydes, as well as long-chain hydrocarbons (Peralta-Ruiz et al., 2018). As far as triglycerides are the main component of vegetable oils and fats, different reactions are used for its processing: hydrolysis, transesterification, hydrogenation, hydrodeoxygenation, etc. Transesterification and hydrodeoxygenation are widely used for the production of renewable fuel (biodiesel, bio-jet, green diesel) (Chen et al., 2015).

In spite of the prevalence of transesterification reaction and its widespread application in the fuel industry, this process has many disadvantages: strong dependence on the feedstock, high oxygen content, low stability, side reactions behavior (in particularly saponification), etc. (Romero et al., 2016). Hydrodeoxygenation is a major way aimed at the solving of transesterification problems. The method allows the formation of diesel-range hydrocarbons in the presence of a heterogeneous catalyst. Hydrodeoxygenation can be considered as one of the reactions of hydrotreatment which take place during the crude oil refinery (de Sousa et al., 2016). Thus, industrial hydrotreatment catalysts (sulfided CoMo and NiMo) are typically used in this process (Zhang et al., 2018). The modern tendencies in the hydrodeoxygenation focused on the search of novel highly active and sulfur-free catalysts (Hachemi et al., 2016). In the example, in the last decades, different Ni-, Pt- and Pd-containing catalysts were developed for hydrodeoxygenation (Stepacheva et al., 2016).

However, hydrodeoxygenation also has some drawbacks which affect the total process cost and, thus, final product compatibility with petroleum fuel. Among such drawbacks, high hydrogen consumption, high temperature, and pressure requirement are the main (Hermida et al., 2015).

The use of supercritical fluids as a medium for the deoxygenation process can significantly decrease the process temperature as well as reaction time. In addition, some compound such as light hydrocarbons, alcohols, and water in the supercritical state can serve as a hydrogen atom donor (Hollak et al., 2014). The last property of supercritical fluids allows the problem of hydrogen consumption to be solved. Nowadays, supercritical water, carbon dioxide, propane, and hexane are most commonly used (Kim et al., 2014). Hexane in the supercritical state is promised to be the most optimal medium for deoxygenation process because it has a relatively low Critical Point ($T_c = 234.5$ °C, $P_c = 3.02$ MPa) and good miscibility with oils at room conditions (Fang et al., 2017).

According to these reasons, n-hexane was chosen as a reaction medium for the supercritical deoxygenation of stearic acid used as a model compound of vegetable oils and animal fats.

2. Experimental

2.1 Materials

Stearic acid ($C_{17}H_{35}COOH$, 99.9 %, ChimMedService, Russia), n-hexane (C_6H_{14} , chemically grade, ReaChim, Russia) were used as received in the experiments. Hypercrosslinked polystyrene (HPS, MN270, non-functionalized, Purolight Ltd., UK) was preliminary washed with acetone and dried at 70 ± 2 °C. Hydrated cobalt and nickel nitrates ($Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, chemically grade, ReaChim, Russia), sodium bicarbonate ($NaHCO_3$, chemically grade, ReaChim, Russia) were used without any pre-treatment for catalyst synthesis.

2.2 Catalyst preparation

The catalysts were synthesized in stainless steel high-pressure reactor Parr-4307 (Parr Instrument, USA) (Figure 1) according to the following procedure (Stepacheva et al., 2018): 1.0 g of HPS pre-treated with acetone, the calculated amount of nickel nitrate and cobalt nitrate, 0.1 g of sodium bicarbonate, and 15 mL of distilled water was placed into the reactor. The reactor was sealed and purged with nitrogen to remove the oxygen. The nitrogen pressure was set at 6.0 MPa. Then, the reactor was heated up to 200 °C and maintained for 15 minutes. After the reaction, the mixture was cooled to room temperature, filtered and washed with distilled water to remove nitrate ions.

The metal content varied from 5 to 15 wt. %. Thus, the catalysts Co-Ni-HPS with different metal loading (5 wt. % Co – 10 wt. % Ni, 10 wt. % Co – 5 wt. % Ni, 10 wt. % Co – 10 wt. % Ni, 15 wt. % Co – 15 wt. % Ni) were obtained.

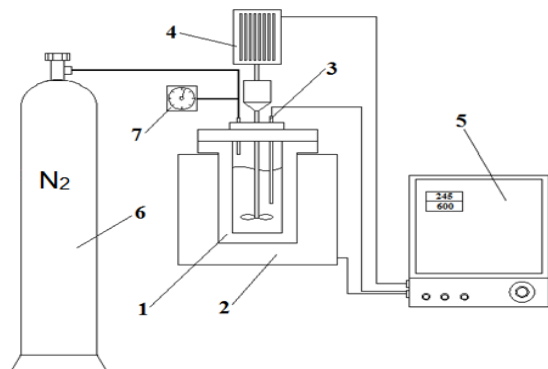


Figure 1: Experimental setup for Co-Ni-HPS catalyst synthesis: high-pressure reactor (1), heater (2), thermocouple (3), stirrer motor (4), control unit (5), nitrogen bottle (6), and manometer (7).

The catalysts were preliminarily reduced in hydrogen flow at 300 °C for 4 hours before the experiments. The catalyst characterization was performed by the low-temperature nitrogen physisorption, X-Ray photoelectron spectroscopy, transmission electron microscopy, and thermogravimetric analysis.

2.3 Deoxygenation process

The process of stearic acid deoxygenation in the medium of supercritical n-hexane was performed in Parr Series 5000 Multiple Reactor System (Parr Instrument, USA) equipped with a magnetic stirrer. In a typical experiment, 30 mL of 0.2 M solution of stearic acid (99.9 %, ChimMedService, Russia) in n-hexane (ReaChim, Russia) with 0.05 g of the catalyst were placed into the reactor. Then the reactor was sealed and heated up to 250 °C in a nitrogen atmosphere (nitrogen partial pressure 3.0 MPa). The total pressure in the reactor after the heating was 6.8 MPa.

The reaction mixture samples obtained after the reaction were analyzed by GCMS using gaseous chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan). The chromatographic column HP-1MS with 30 m length, 0.25 mm diameter and 0.25 μ m film thickness were used for the analysis. The column temperature was programmed as follows: initial temperature of 150 °C was maintained for 6 min then the temperature was raised up to 300 °C with the heating rate of 15 °C/min and maintained at 300 °C for 5 min. Helium with the volumetric velocity of 20.8 mL/s and pressure 253.5 kPa was used as a gas-carrier. The

injector temperature was 280 °C, ion source temperature was 260 °C; interface temperature – 280 °C; scanning was performed from 10 to 800 m/z; scanning rate – 625; electron impact ionization.

3. Results and discussion

3.1 Deoxygenation results

Four bimetallic catalysts were tested in the stearic acid deoxygenation process in supercritical n-hexane: 5 % Co-10 % Ni-HPS, 10 % Co-5 % Ni-HPS, 10 % Co-10 % Ni-HPS, 15 % Co-15 % Ni-HPS. The experimental data on the catalyst influence on the stearic acid conversion and product yield are shown in Figures 2 and 3. It is well seen, that the catalysts allow full substrate conversion to be reached within 1 h of the process (Figure 2). Noteworthy, that the increase in the nickel content increases the substrate conversion rate, while cobalt content practically does not affect the substrate consumption. The data observed can be explained by the higher impact of nickel in the deoxygenation reaction.

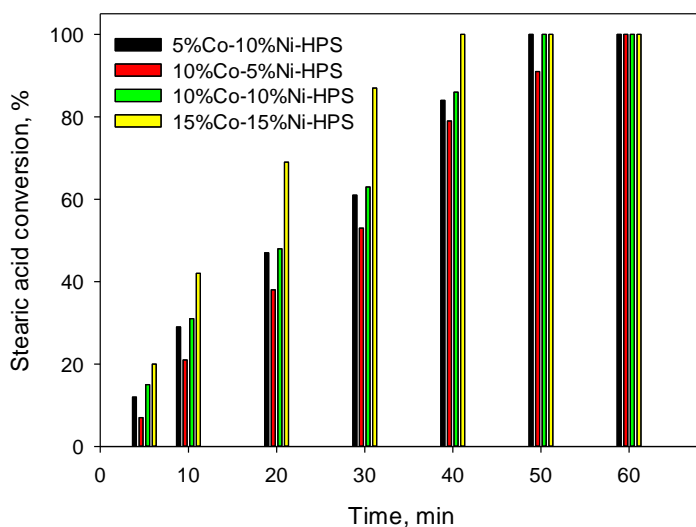


Figure 2: Catalyst influence on stearic acid conversion.

The influence of the catalyst composition on the product yield at full substrate conversion is presented in Figure 3. The liquid phase analysis showed that n-heptadecane was the major reaction product, however, the formation of lower hydrocarbons (C_{10} - C_{16}) was also observed.

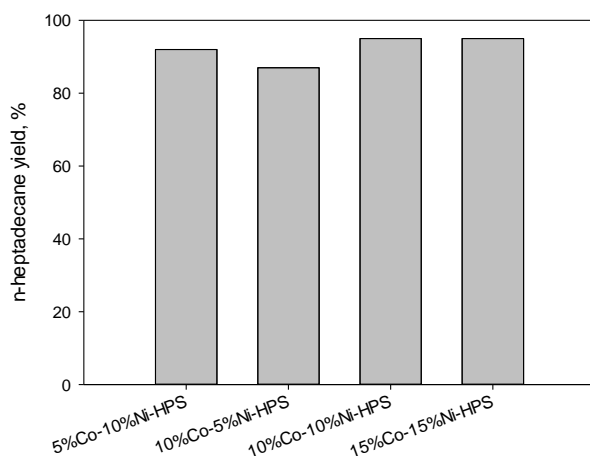


Figure 3: Catalyst influence on heptadecane yield.

It is well seen that the increase in cobalt content leads to an increase in n-heptadecane yield decreasing the formation of lower hydrocarbons. However, the decrease in nickel loading in the catalyst (in the case of 10 % Co-5 % Ni-HPS) decreases the target product yield. Such a decrease can be explained by the formation of unsaturated C₁₇ hydrocarbons, while Ni catalyzes their hydrogenation. Thus, it can be proposed that cobalt promotes the formation of long-chain hydrocarbons, while nickel accelerates its hydrogenation.

Based on the catalyst testing results 10 % Co-10 % Ni-HPS was chosen as the most optimal catalyst for the stearic acid deoxygenation in the medium of supercritical n-hexane allowing reaching 95 % yield of n-heptadecane at full substrate conversion within 50 min of the experiment. The chosen catalyst was analyzed using physics-chemical methods.

3.2 Catalyst characterization

In order to analyze the structure of the optimal catalyst, the measurements of porosity, thermal stability, active phase particle size, and surface composition were performed. Thermal stability was studied using TG 209 F1 (NETZSCH, Germany) thermoscales. The thermograms of the support before and after treatment with overheated water are shown in Figure 4. The similarity of the weight loss curves indicates the absence of any changes in the polymer composition of the support after hydrothermal treatment.

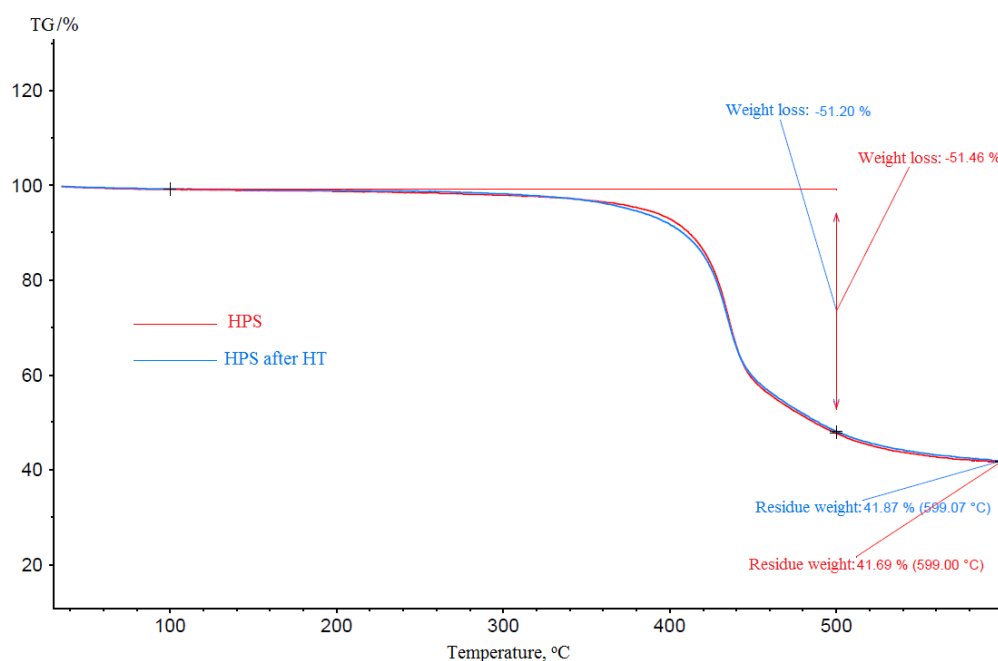


Figure 4: HPS thermograms: (a) initial sample, (b) after treatment in hydrothermal conditions.

In order to evaluate the porosity of the synthesized catalysts, low-temperature nitrogen physisorption was carried out using analyzer Beckman Coulter™ SA 3100™ (Coulter Corporation, USA). The analysis of the nitrogen adsorption isotherms showed that the hydrothermal treatment of the support leads to the formation of mesopores with mean diameter 20-50 nm while the initial support has micropores with mean diameter 4-6 nm (Figure 5). It is noteworthy, that the surface area of the support after the treatment in hydrothermal conditions slightly decreases (1400 and 1250 m²/g for initial HPS and HPS treated with overheated water respectively). Metal deposition on the surface of the polymeric support in hydrothermal conditions did not lead to a significant decrease in the surface area (1100 m²/g for 10 % Co-10 % Ni-HPS catalyst). This indicates fine active phase distribution on the internal and external surface of the support and the absence of the pore blockage with the active phase particles that is also confirmed by close values of total pore volume (0.98, 1.00, 0.99 mL/g for initial HPS, treated HPS, and Co-Ni-HPS, respectively) (Smirnova et al., 2009).

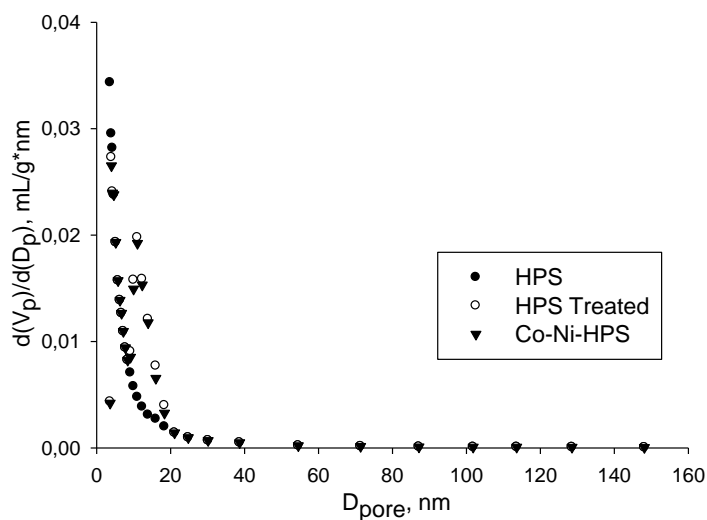


Figure 5: Pore size distribution for the initial support, treated support and resulted catalyst.

In order to estimate the surface elemental composition and metal state, the XPS analysis was performed using electron spectrometer ES – 2403 (SCB AE RAS, Russia) equipped with the analyzer of energies PHOIBOS 100-5MCD (Specs GmbH, Germany) and X-Ray source MgK α /AlK α XR-50 (Specs GmbH, Germany). Survey spectra analysis showed that during the HPS treatment with overheated water, the concentration of the surface contaminants (S, Cl, N, Si) decreased sufficiently in comparison with the initial support. The absence of nitrogen indicated the full hydrolysis of nitrates during the catalyst synthesis. The analysis of high-resolution spectra for Ni 2p and Co 2p (Figure 6) allows concluding the formation of nickel and cobalt hydroxides on the support surface. Thus, the active phase is presented by a mixture of NiOOH and Co(OH) $_2$. The strong shift of binding energies indicates the formation of a thin layer of the active phase on the polymer surface (Grossvenor et al., 2006).

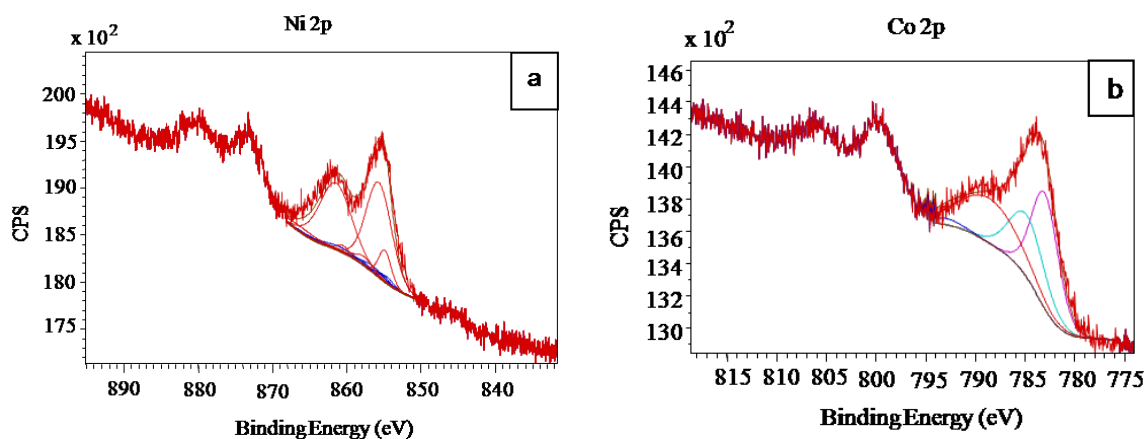


Figure 6: High-resolution spectra of Ni 2p (a) and Co 2p (b) sublevel.

Fine distribution of the active phase particles was confirmed by the transmission electron microscopy performed using JEM1010 scanning transmission electron microscope (JEOL Ltd., USA). The mean diameter of the active phase particles was found to be 6 ± 0.1 nm. It is noteworthy that the catalyst reduction does not lead to the particle aggregation that indicates the stability of the active phase.

Thus, the catalyst analysis showed that the hydrothermal synthesis allows obtaining a bimetallic catalyst with a fine distribution of the active phase. High activity of the catalysts in stearic acid deoxygenation can be explained by the formation of large pores during the synthesis which allows acceleration of substrate molecule adsorption on the catalyst surface and facilitates the access of substrate molecules to the active sites of the catalyst.

4. Conclusions

In this paper, the bimetallic Co-Ni-containing catalysts synthesized by the hydrothermal deposition in the supercritical fatty acid deoxygenation were studied. Four samples – 5 % Co-10 % Ni-HPS, 10 % Co-5 % Ni-HPS, 10 % Co-10 % Ni-HPS, 15 % Co-15 % Ni-HPS – were tested in stearic acid deoxygenation in the medium of supercritical n-hexane. It was found that cobalt promotes the formation of long-chain hydrocarbons, while nickel accelerates its hydrogenation by hydrogen atoms donated by the solvent in the supercritical state. 10 % Co-10 % Ni-HPS was chosen as the most optimal catalyst for the stearic acid deoxygenation in the medium of supercritical n-hexane allowing reaching 95 % yield of n-heptadecane at full substrate conversion within 50 min of the experiment. The hydrothermal synthesis allows obtaining a bimetallic catalyst with a fine distribution of the active phase and leads to the formation of large pores which facilitate the access of substrate molecules to the active sites of the catalyst.

Acknowledgments

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