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Novel Catalyst Synthesized by Hydrothermal Method for Fatty Acid Conversion into Hydrocarbons

Antonina A. Stepacheva[a], Mariia E. Markova[b], Valentina G. Matveeva[a], Mikhail G. Sulman[a], Esther M. Sulman[a]

[a]Tver State Technical University, A. Nikitin str., 22, Tver, 170026, Russia
[b]Tver State University, Zhelyabova str., 33, Tver, 170100, Russia
a.a.stepacheva@mail.ru

Here, the novel method for the conversion of fatty acids into hydrocarbon fuel without hydrogen consumption is reported. The deoxygenation of stearic acid as a model compound was performed in the medium of supercritical n-hexane in the presence of Ni-containing catalysts synthesized by a hydrothermal deposition method. We studied the influence of the support as well as the metal loading on the yield of target products of stearic acid conversion into hydrocarbons. Ni was supported on the three different supports: anhydrous microporous silica, anhydrous alumina, and non-functionalized hypercrosslinked polystyrene. The hydrothermal synthesis of the catalysts leads to the changes in the porosity and structure of the supports increasing the number of mesopores. The active phase of the catalysts was found to be deposited on the internal surface of the supports as a thin layer of γ-NiOOH. Ni/HPS catalyst was found to be the most active in the stearic acid deoxygenation process in supercritical n-hexane. The study of the influence of the metal loading on the conversion of the substrate and the target product yield showed that 10 wt. % of Ni is more favorable for the production of high yield of C_{16}-C_{17} hydrocarbons.

1. Introduction

The limitation of fossil energy sources leads to the growth of interest in renewable fuels. Biomass is the most permissive resource for the production of energy (Meller et al., 2014). Different compounds of plant biomass such as cellulose, lignin, hemicelluloses, and vegetable oils have attracted great attention of the researchers (Niemantsverdriet et al., 2017). Nowadays triglycerides are one of the most available renewable feedstock for the production of biofuels (Peralta-Ruiz et al., 2018). The transesterification of vegetable oils is one of the most commonly used ways for biodiesel production. However, its cost strongly depends on the cost of the feedstock. From this point of view, the use of non-edible or waste oils is the most prospective. In spite of the numerous studies, the problems of the transesterification of such cheap oils are the largest challenge for chemical engineering. Such parameters as water and free fatty acid content in the feedstock, as well as the presence of different contaminants, strongly affect the final fuel as well as the conversion degree (Romero et al., 2016).

One of the alternatives to transesterification is deoxygenation of vegetable oils and their components. This process allows solving the main problems of the classical transesterification resulting in the production of fuels with lower acidity, lower viscosity and higher cetane number (up to 99) (de Sousa et al., 2016). The oxygen removal from the triglycerides through deoxygenation proceeds over conventional NiMo/Al_2O_3, CoMo/Al_2O_3 (Zhang et al., 2018) or noble metal (Pt/C, Pd/C) (de Sousa et al., 2016) catalysts. However, in order to obtain saturated oxygen-free compounds, the use of a sufficiently high amount of hydrogen is required. The high hydrogen consumption leads to a sufficient increase in the deoxygenation cost making the resulted fuel uncompetitive (Hermida et al., 2015).

From this point of view, the decarboxylation process consisting of removal of oxygen in the form of CO_2 is more preferable than deoxygenation. This way requires the use of highly selective catalyst allowing producing a high yield of the target product. Typically, noble metal catalysts such as Pd/C (Hollak et al., 2014), Pt/C (Kon

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et al., 2014), Pt/zeolite (Santillan-Jimenez et al., 2014), Pt/TiO_2 (Ma and Zhao, 2015), etc. are used for decarboxylation. Recently, we also reported Pd/HPS as an effective deoxygenation catalyst (Stepacheva et al., 2016). However, these catalysts often have high selectivity to the formation of alkenes. This leads to the need in the additional hydrogenation step. Moreover, the decarboxylation process is carried out in either non-solvent medium or in the presence of C_{10}-C_{12} hydrocarbons which have significantly high density and, thus, require higher temperatures.

In order to make the decarboxylation process low-cost, the numerous researchers proposed the use of sub- and supercritical solvents. Such an approach allows decreasing the process temperature (depending on the solvent used). Moreover, the supercritical conditions allow sufficiently decreasing the process time (several minutes vs. several hours). Besides, some solvents in sub- or supercritical conditions can be hydrogen donors, thus, allowing the additional upgrading of the products. According to the literature, n-hexane is the most suitable solvent for supercritical deoxygenation (Kim et al., 2014), since it forms a homogeneous phase with oil at room temperature and provides both a high conversion of the feedstock and the yield of the target product (Fang et al., 2017). Moreover, the use of supercritical n-hexane allows the process to be carried out in milder conditions.

Another direction for the decrease in the process cost is the use of cheaper catalysts (Kubička et al., 2014). Some works are devoted to the application of Ni-containing catalysts which showed high activity and selectivity in the deoxygenation of oils (Chen et al., 2015) and fats (Hachemi et al., 2016). However, the existing methods of the catalyst preparation have numerous disadvantages such as active phase aggregation, non-uniform particle distribution, pore blockage, etc. Last decades, the hydrothermal catalyst synthesis in the medium of the superheated water is of great attention (Zhang and Erkey, 2006). Because of its unique properties subcritical water allows the formation of the metal nanocrystals without using surfactants and ligands preventing the nanoparticle agglomeration (Morère et al., 2011). Such approaches allow controlling the metal particle size and morphology. The low surface tension of the near critical water also prevents the pore blockage and enhances the diffusion of the metal precursor solution into the pores of the support.

In the current work we synthesized Ni-containing catalysts on the inorganic (silica, alumina) and polymeric (hypercrosslinked polystyrene) supports by the hydrothermal method. The catalysts were studied in the stearic acid deoxygenation in the medium of supercritical n-hexane in order to obtain hydrocarbon fuel with a high cetane number.

2. Experimental

2.1 Catalyst Preparation

The Ni-containing catalysts were synthesized by the hydrothermal deposition of the metal precursors (nickel nitrate) in the pores of the support in a laboratory set-up (Figure 1) according to the procedure described in our previous work (Stepacheva et al., 2018).

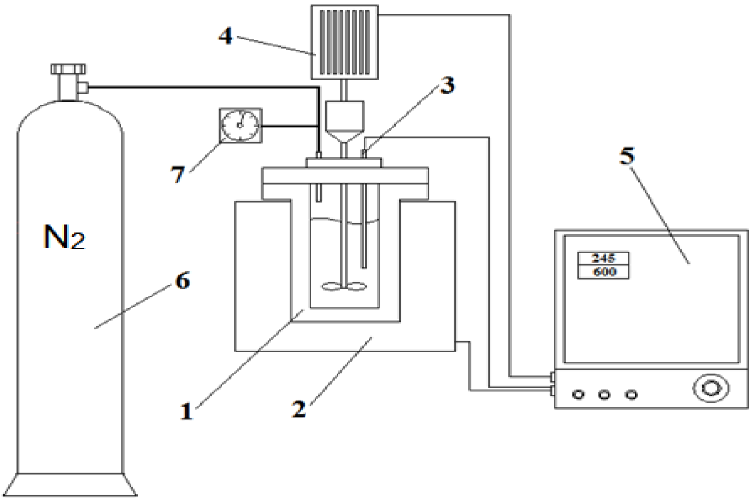

Figure 1: Laboratory setup for catalyst synthesis: high-pressure reactor (1), heater (2), thermocouple (3), stirrer motor (4), control unit (5), nitrogen bottle (6), and manometer (7).

Ni-compounds were deposited on the three different supports: anhydrous microporous silica (SiO_2, Reachim, Russia), anhydrous alumina (Al_2O_3, Kupavna reactive, Russia), and non-functionalized hypercrosslinked polystyrene (HPS, Purolight Inc., UK). All the supports were preliminarily dried at 70 °C for 90 min. After the choice -of the optimal support, the Ni loading was varied from 5 to 20 wt. %.

2.2 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 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. In order to exclude the equilibrium shift, the process was performed varying time from 5 to 60 min with 5 min interval.

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 µm film thickness were used for the analysis.

3. Results and Discussion

3.1 Support Influence

In order to evaluate the influence of the support, three types of porous materials were chosen: microporous silica, alumina, and HPS. The data on the support effect on the stearic acid deoxygenation in supercritical n-hexane are presented in Figure 2. It is well seen, that the HPS –based catalyst provides a higher rate of stearic acid conversion. The catalysts supported on silica and alumina showed practically equal rates of substrate consumption. It is interesting to note a slight decrease in the stearic acid conversion rate for the silica-based catalyst.

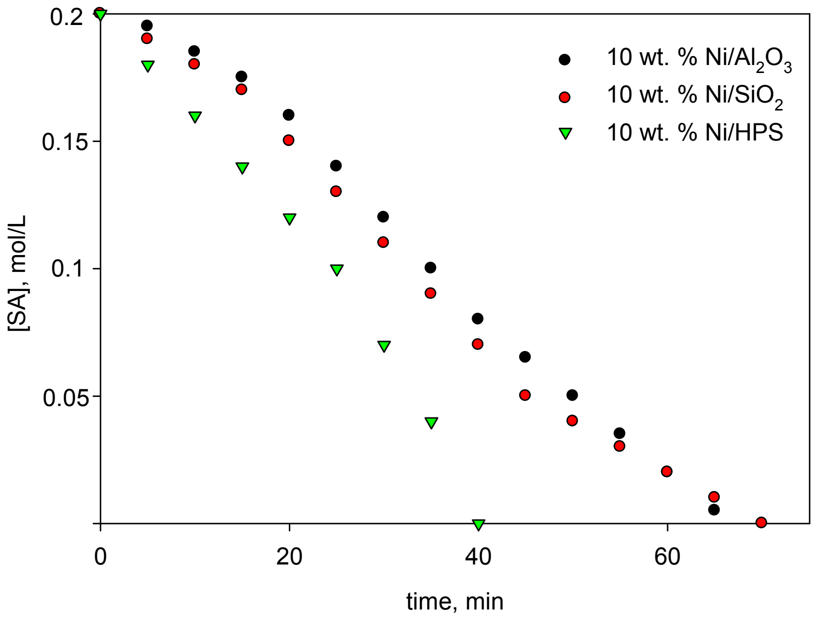

Figure 2: Influence of the support on the stearic acid consumption.

For a better understanding of the obtained results, the physical-chemical analysis of the catalysts was performed (Table 1). It is seen that the hydrothermal synthesis of the catalysts leads to the decrease in the micropore surface area forming mesopores with the diameter above 10 nm. Such mesoporous materials are more preferable for the conversion of large molecules (e.g. stearic acid and triglycerides). HPS-based catalyst has the highest surface area which allows higher adsorption of the substrate molecules and, thus, higher conversion rate. Moreover, the hydrophobes character of this support is more preferable for the reactions in the medium of non-polar solvents. A sharp decrease in the total surface area for silica-based catalysts caused by the support recrystallization in the superheated water allows proposing the full saturation of the catalyst surface and the decrease in the reaction rate at the end of the deoxygenation.

Table 1: Catalyst characterization results

Catalyst	Surface area, m^2/g	The surface area of micropore, m^2/g	Average pore diameter, nm	Acidity, mmol/g	Metal concentration, wt. %	Metal compound
SiO_2	390	121.0	5.0	0.53	-	-
Ni/SiO_2	125	5.5	20-30	0.45	5.8	γ-NiOOH
Al_2O_3	420	95.0	8.5	0.34	-	-
Ni/Al_2O_3	240	10.0	15-20	0.25	6.3	γ-NiOOH
HPS	1370	900.0	4.5	-	-	-
Ni/HPS	1220	650.0	10-20	-	6.1	γ-NiOOH

The high acidity of the alumina and silica supports (Table 1) also leads to the acceleration of cracking reaction and the formation of C_{10}-C_{16} hydrocarbons (see Figure 3). The highest selectivity to n-heptadecane (over 90 wt. %) was observed while using Ni/HPS catalyst. This catalyst also showed high stability in the deoxygenation process as it was shown recently (Stepacheva et al., 2018). Thus, Ni supported on HPS was chosen for further investigation.

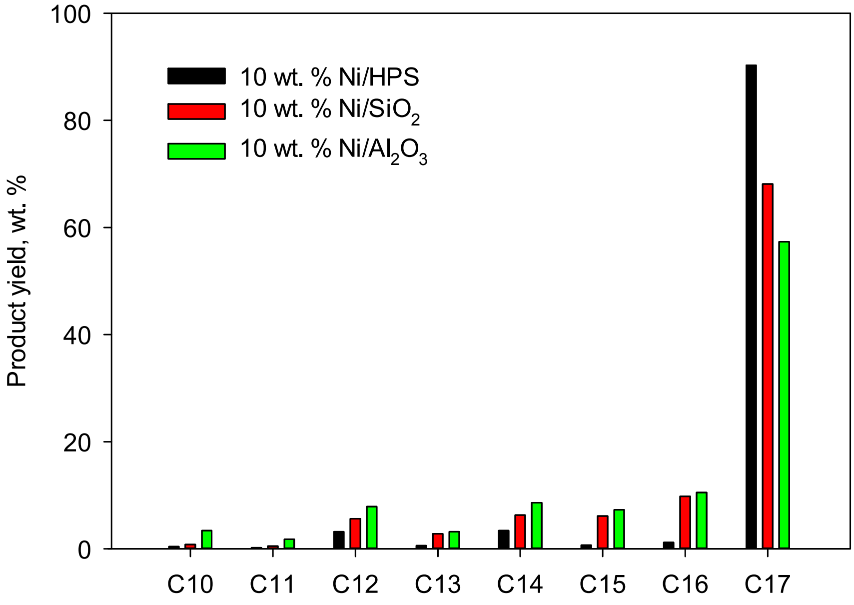

Figure 3: Influence of the support on the deoxygenation product distribution.

3.2 Ni Loading Influence

In order to estimate the influence of Ni loading on the stearic acid deoxygenation in supercritical n-hexane, the experiments on the variation of Ni content in the catalyst from 5 wt. % to 20 wt. % were carried out. Figure 4 shows the stearic acid consumption curves depending on Ni loading. It is well seen that the increase in Ni content leads to an increase in the deoxygenation rate. However, the relative reaction rates for 10 wt. % Ni/HPS and 15 wt. % Ni/HPS are close to each other. This may be due to the practically equal accessibility of the active sites in the catalysts. The 20 wt. % Ni/HPS showed the highest rate of stearic acid consumption allowing full substrate conversion at 30 min. However, the study of the influence of Ni content on the n-heptadecane yield (Figure 5) showed that the concentration of Ni above 10 wt. % does not affect the target product yield. Thus, the increase in the Ni content is not preferable from the point of view of the process cost.

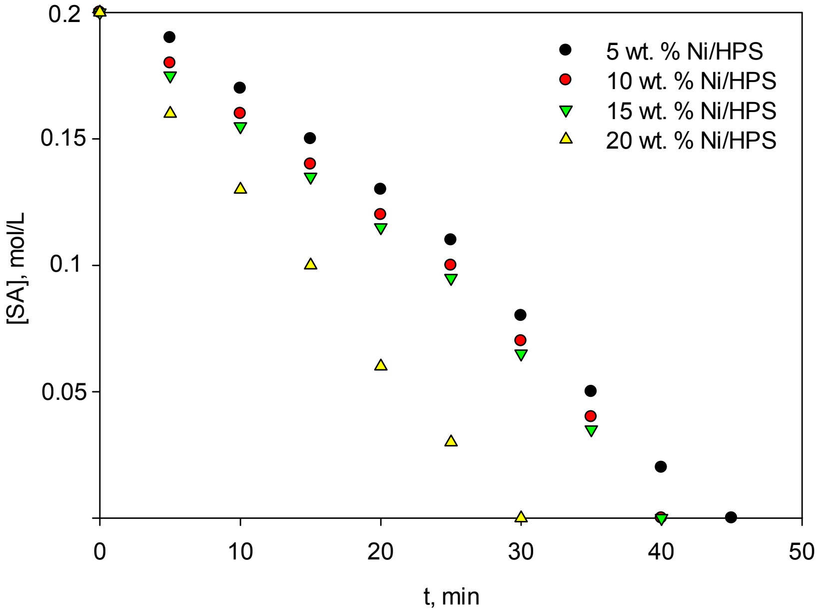

Figure 4: Influence of Ni loading on the stearic acid consumption.

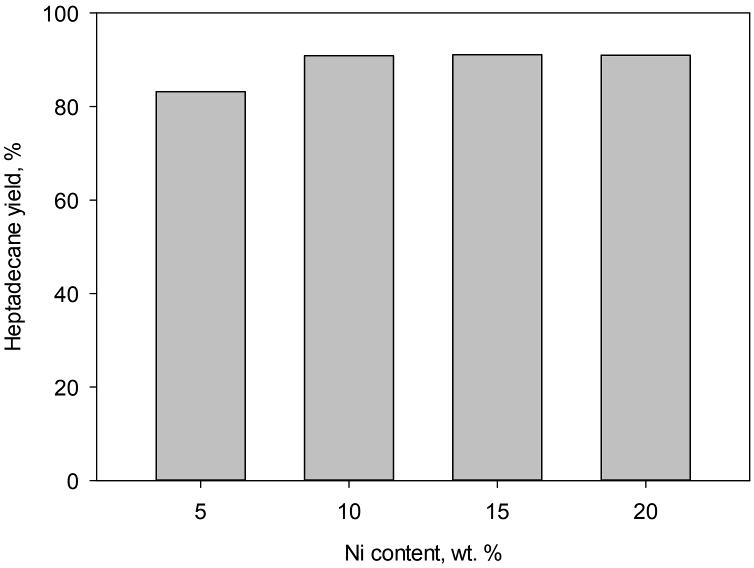

Figure 5: Influence of Ni loading on the n-heptadecane yield.

4. Conclusions

In the current work, the study of the Ni-containing catalysts synthesized by the hydrothermal deposition on the stearic acid deoxygenation in the medium of supercritical n-hexane was performed. The influence of the catalyst support and Ni loading on the deoxygenation rate and product yield was studied. It was shown that 10 wt. % Ni/HPS was found to be the most effective catalyst allowing obtaining over 90 wt. % of n-heptadecane yield at full stearic acid conversion. The analysis of the synthesized catalysts showed that the hydrothermal synthesis leads to the changes in the porosity and structure of the supports increasing the number of mesopores. The active phase of the catalysts was found to be presented by a thin layer of γ-NiOOH.

Acknowledgments

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