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Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel

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ABSTRACT

The investigation of upgraded bio-fuels production processes was carried out via the development of efficient catalysts for oxy-organic hydrodeoxygenation (HDO) processes. It was found that Ni–Cu catalysts are more attractive than single Ni catalysts in HDO under mild conditions. Copper facilitates the nickel oxide reduction at temperatures lower than 300 °C. Moreover, copper prevents methanization of oxy-organics at 280–350 °C. The catalyst supports play also a key role in hydrotreatment of oxygen-containing compounds. Screening of catalyst supports showed that CeO_2 and ZrO_2 are most effective in the target processes because of possible additional activation of oxy-compounds on the support surface. The prepared catalysts have non-sulfided nature and can be used for upgrading of bioliquids with a low sulfur content.

1. Introduction

The petroleum consumption has surged during the 20th century, at least partially because of the rise of the automobile industry. Today, fossil fuels such as coal, oil and natural gas provide more than three quarters of the world's energy consumption. On the other hand, biomass of plants can serve as a source for both energy and motor fuels, and being renewable it is the only sustainable source of energy and hydrocarbons for industry and automobile society. At present, biodiesel and bioethanol can be a substitute for the conventional fuels. The other promising feedstock for the engine fuels' production is bio-oil—the liquid product of biomass flash pyrolysis [1]. However, this crude bio-oil cannot be used directly as a fuel for spark engines because of its poor operational characteristics. The main reason of low quality of bio-crude-oil is the high content of oxygen. And whereas biodiesel and bioethanol can serve as improving additives to the conventional hydrocarbon fuel, in the case of pyrolysis oil, its catalytic pretreatment is required for the removal of oxygen and increasing the content of hydrogen in the liquid.

Recently, a number of publications appeared in the field of hydrodeoxygenation (HDO) of the esters of fatty acids (biodiesel) [2–5]. These studies were initiated by the need for upgrading biodiesel and bio-oil as fuels for spark engines. The majority of researchers use conventional hydrodesulfurization (HDS) catalysts—sulfided Co–Mo and Ni–Mo supported on alumina—for the HDO reaction. However, the employment of HDS catalysts requires the addition of sulfur-containing compounds, for example H_2S or thiophene, in the reaction zone for keeping the catalysts in the active form.

Numerous studies on catalytic HDO of bio-crude-oil were reviewed in detail by Bridgwater et al. [6] and Elliott [7]. The HDO of pyrolysis liquid is commonly carried out in the presence of sulfided Co–Mo and Ni–Mo catalysts, as in the case of biodiesel.

It should be noted that conventional HDS catalysts for oil refinery are not suitable for the bio-crude-oil or biodiesel hydrotreating because of a low sulfur content in the initial bio-feedstock. This is caused mainly by the reduction of sulfided Co or Ni catalysts to the metal state followed by the coke formation and catalyst deactivation. Desulfurization of the catalyst can be prevented by the addition of sulfur donor compounds to the feedstock. In this case, sulfur is converted to H_2S, which is removed from hydrogenated products. The use of the non-sulfided catalysts allows elimination of this sulfurization step.

Thus, the main aim of this work was the development of non-sulfided catalysts for the upgraded bio-fuels production. The HDO reaction was studied with biodiesel and anisole. Anisole was chosen as a model compound for bio-crude-oil since its structure is similar to the main products of the lignin depolymerization during fast pyrolysis of wood. Phenol derivatives are considered to be the

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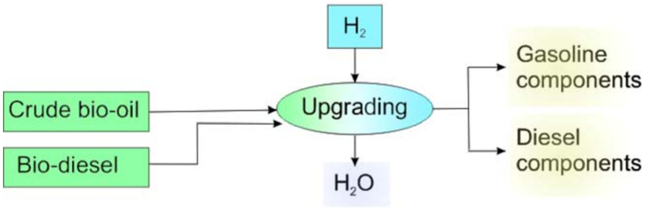


Scheme 1. The developing pathways of the upgraded bio-fuels production from bioliquids.

most stable components of bio-crude-oil. Thus, high stability of anisole in hydrogenolysis reactions determined the choice of this compound as a model for HDO tests.

A schematic representation of the upgraded bio-fuels production is shown in Scheme 1.

The development of new catalysts for the reductive bioliquids upgrading was based on the idea that promising catalysts for this process should be bifunctional. On one hand, an oxide form of a transition metal with variable valence is needed for the activation of oxy-groups in the oxygen-containing compounds in bio-crude-oil. On the other hand, a transition metal in its reduced state is required to activate dihydrogen. It must be taken into account that the catalyst is able to deactivate due to the coke formation; therefore the reaction temperature should not exceed 350–400 °C and the dihydrogen pressure should be as high as 8.0–10.0 MPa. The oxides of such metals as Mo, W, Co, Mn, Zr, Ce, Y, Sr and La possess the mobile oxygen under the indicated conditions. Thus, these oxides may be used for the activation of oxygen-containing compounds. Noble metals (Pt, Pd, and Rh) are commonly used for the hydrogen activation [8]. However, since the HDO of bioliquids is expected to be a large-scale process, employment of the noble metal-based catalysts could significantly raise the cost of the processing. In this connection, it seems more reasonable to use Ni-based catalysts for the process since these are also able to activate dihydrogen under the reaction conditions indicated above.

2. Experimental

2.1. Oxy-organic substrates

In this study, anisole ($C_6H_5OCH_3$) from Sigma Co. and biodiesel produced from the rapeseed oil (Czech Republic) were employed as the initial oxygen-containing substrates for studies of the HDO processes. The composition of biodiesel was as follows: oleic acid methyl ester (59%), linoleic acid methyl ester (20%), stearic acid methyl ester (10%), linolenic acid methyl ester (8%) and erucic acid methyl ester (3%).

2.2. Catalysts and their preparation methods

In the present work, Rh-, Rh–Co-, Ni- and Ni–Cu-containing catalysts were tested in the HDO. SiO_2, Al_2O_3, ZiO_2, CeO_2, CeO_2–ZrO_2 were used as catalyst supports. Commercial SiO_2 and Al_2O_3 were received from the Sasol Company. ZiO_2, CeO_2, and CeO_2–ZrO_2 supports were prepared at the Boreskov Institute of Catalysis (Russia).

The catalysts were synthesized by wet impregnation of the support with aqueous solutions of the active metal salts or by co-precipitation method. In the case of the impregnated catalysts, the support was spherical Al_2O_3 of 1.8 mm diameter. Before the impregnation, Al_2O_3 was calcined in air at 1000 °C, after the calcination its BET surface area was ca. 100 m^2/g. The prepared catalysts were crushed and sieved to a fraction of 0.25–0.5 mm. In the case of the co-precipitation catalysts, a NaOH solution (1N) was added under vigorous stirring to a solution of metal salts at 70 °C, pH of the solution was maintained at 10. The precipitates were aged for 5 h under the same conditions, filtered, washed with water and dried at 100 °C for 12 h. The dried samples were calcined at 500 °C for 6 h in air. The catalysts were activated before the reaction by reduction under the following conditions: $T = 300$ °C at 1 MPa of H_2 for 1 h. The data on the catalysts composition were obtained by the elemental analysis.

The Rh content in the prepared catalysts was 0.5 wt.%. In the case of Ni–Cu catalysts, the total percentage of Ni and Cu was 38 wt.% with the Ni:Cu molar ratio equal to 3:1. The single Ni catalysts contained 38 wt.% of nickel. The specific surface areas (A_{BET}) of the prepared catalysts were 120–130 m^2/g for the catalysts supported on SiO_2 and Al_2O_3, and 140–150 m^2/g for the catalysts supported on CeO_2, ZrO_2, and CeO_2–ZrO_2.

2.3. Catalysts characterization

The specific surface area of catalysts was determined by BET methods from the data on nitrogen adsorption measured at 77 K with an automatic volumetric device ASAP 2400.

The XRD analysis was performed on the D500 Siemens (Germany) X-ray diffractometer using the Cu Kα radiation. The diffraction patterns were recorded by scanning with 0.05° step at the angle range from 30 to 80° and accumulation period of 5 s at each point. The high-temperature *in situ* XRD experiments were performed using the reactor chamber [9]. The gas flow (hydrogen) was fixed at 600 cm^3/min, the heating rate was 25 °C/min. The hydrogen pressure was 0.1 MPa. The samples were heated in the hydrogen atmosphere to 300 °C. Then XRD patterns were recorded by scanning on 2θ from 30° to 55° at 300 °C until the sample achieves a quasi-equilibrium state and its diffraction pattern does not change. Then the samples were cooled in hydrogen atmosphere and XRD patterns were recorded. The average sizes of crystallites were calculated using the Sherrer equation.

2.4. HDO reaction conditions

HDO of oxy-organic compounds was carried out under isothermal conditions at 250–400 °C and total pressure of 0.5–2.0 MPa. The reaction was performed in the flow fixed-bed reactor with internal diameter 5 mm. The reactor was packed with 0.5 ml of a catalyst diluted with 1 ml of quartz sand (0.25–0.5 mm fraction). The feed gas was a mixture of H_2 (50 vol.%) and Ar (50 vol.%), with the feed rate of 20 L h^{-1}. LHSV was equal to 1–6 h^{-1}.

2.5. Product analysis

Liquid products (organics and water) were collected in a trap cooled with ice every 30 min in the case of the anisole HDO and every 60 min in the case of the biodiesel HDO. The liquid products were analyzed with a gas chromatograph (Hromos GH-1000, Russia) equipped with a FID (300 °C) and a capillary column (Zebron ZB-1, stationary phase 100% dimethylpolysiloxane, 0.25 μm × 0.32 mm × 30 m). The gaseous products were analyzed with a gas chromatograph (Hromos GH-1000) equipped with FID and TDC detectors and packed columns (stationary phases Silohrom and activated carbon). The HDO degree corresponds to the selectivity of hydrogenated products formation:

$$\mathrm{HDO}\,(\%) = \frac{\sum_i C'_i}{\sum_i C_i} \times 100,$$

where C'_i is the concentration of the oxygen-free product i, while C_i is the concentration of any product i. The specific catalytic activity was defined as the oxygen-free products formation rate (mol h^{-1}) divided by Ni mass (g) in the Ni-based catalyst sample.

3. Results and discussion

3.1. HDO of anisole

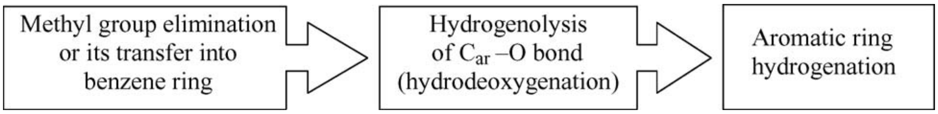
The first test on the anisole HDO showed a low HDO degree when the commercial sulfided Ni–Mo and Co–Mo catalysts (Albemarle Co.) were used under mild conditions (250–350 °C, 1.0 MPa). For example, at 300 °C and 1.0 MPa of H_2 in the presence of sulfided $CoMo/Al_2O_3$, the following reaction products were obtained: 41 mol.% phenol, 23% benzene, 5% cyclohexane and ca. 30% methylphenols isomers. In the case of sulfided $NiMo/Al_2O_3$, the selectivity of the oxygen-free products formation was still lower, 15%. Therewith, a rapid deactivation of the catalysts due to the coke formation was observed. The oxidized Co–Mo or Ni–Mo catalysts did not give satisfactory results. In the presence of the oxidized catalysts at the 100% conversion of anisole, the main products were phenol (ca. 40 mol.%) and anisole isomerization products (ca. 60%): isomers of mono-, bi-, tri- and tetra-methylphenols. Therefore, we decided to use non-sulfided heterogeneous catalysts for hydrogenolysis. At first, some Rh-based catalysts with the active metal content of 0.5 wt.% were prepared. Rh is generally known to be one of the most efficient dihydrogen activation agents; as a result, rhodium is used as an active component of catalysts for a wide range of hydrogenation reactions. The results of the Rh-based catalysts screening are presented in Table 1. The probes for analysis were taken after 60 min of the reaction.

One can see that bimetallic catalysts are more active in HDO of anisole than monometallic catalysts. This fact confirms the hypothesis that the HDO reaction requires at least two types of active sites: one for the activation of dihydrogen, while the other—a metal with a variable oxidation state (Co, Ce and Zr)—for the activation of oxy-groups. The results of the tests showed also an intensive coke formation in the case of γ-Al_2O_3 due to the presence of weak Lewis-type acidic sites on its surface. In addition, a high selectivity of the methyl transfer to benzene ring that occurs on alumina can also be attributed to acidity of Al_2O_3. Although the anisole conversion was high, however, alumina itself has no HDO activity, so the main products were phenol and its derivatives. Since acidity of alumina is undesirably high for the target reaction, for further experiments, Al_2O_3 used as the support was calcined at 1000 °C during 2 h to form δ-Al_2O_3. After the calcination, the BET surface area was ca. 100 m^2/g.

The employment of inexpensive Ni instead of Rh as HDO catalyst can decrease considerably the HDO process cost, so the next series of catalysts was prepared with Ni. It is well known that Ni catalysts are also active in hydrogenation [10–14]. Ni-based catalysts are also suitable for the HDO reactions. High temperatures (350–400 °C) and hydrogen pressure (up to 12 MPa) are required for high process efficiency [7]. As far as the aim of the present work was to develop a non-sulfided heterogeneous catalyst that would be active and stable in HDO, a series of Ni catalysts supported on various carriers (δ-Al_2O_3, ZrO_2, CeO_2 and SiO_2) were prepared. A number of catalysts were doped with Cu, since in the presence of copper, the nickel oxide reduction occurs at lower temperatures compared to the single nickel oxide [15]. The results of the HDO tests are presented in Table 2.

As follows from Table 2, the Ni–Cu catalysts seem to be more active in the anisole HDO than single Ni catalysts. Over Ni/Cr_2O_3, the main product was cyclohexanol (ca. 80%), whereas C_{ar}–O bond hydrogenolysis products formed only in small quantities. In this case, the hydrogenation of aromatic ring was predominant. The highest HDO degrees were observed for bimetallic systems supported on δ-Al_2O_3 and CeO_2.

The data obtained indicate that hydrotreating of anisole proceeds in the following order:



The catalyst activity determines the conversion degree of the reactants. In the anisole HDO, the specific catalytic activity, normalized to the nickel content in the catalyst, decreases with the Ni content rising; this may result from decreasing of the nickel species dispersion.

Some of the mentioned catalysts were also tested in the real bio-crude-oil (VTT, Finland) HDO at the University of Groningen, The Netherlands. The results showed the possibility of a substantial decrease of the oxygen content in bio-crude-oil, from ca. 40 wt.% to 5 wt.%.

3.2. Hydrotreatment of biodiesel

At present, biodiesel—a product of the fatty acids triglycerides (vegetable oils and fats) transesterification by methyl alcohol—is produced on industrial scale and is used as an additive to fossil diesel fuels. However, the biodiesel content in the mixed fuel is usually less than 20% because of its undesirable properties that impose considerable limitations on the biodiesel employment. There are evidently two pathways to increase the biodiesel proportion in the mixture with fossil fuel: a modernization of the internal combustion engine or upgrading the biodiesel. Biodiesel upgrading consists in the removal of oxygen-containing functional groups. As it was mentioned above, deoxygenation of FAME is commonly carried out in the presence of sulfided HDS catalysts [5] or, more frequently, using noble metals supported on carbon [2–4].

In order to test the possibility of the non-noble and non-sulfided catalysts employment for the biodiesel upgrading, a series of experiments were conducted. The same approach to the catalysts design as in the case of bio-crude-oil model compound HDO was applied. Single Ni and Ni–Cu systems were used as active components for the hydrogen and organics activation.

Table 1
Rh-based catalysts in the anisole hydrodeoxygenation at 300 °C and 1.0 MPa of H_2.

Catalyst	Rh/SiO_2	$RhCo/Al_2O_3$	$Rh/CoSiO_3$	$RhCo/SiO_2$	Co/SiO_2	Rh/ZrO_2	Rh/CeO_2	Al_2O_3
LHSV (h^{-1})	0.3	0.3	0.5	0.3	0.3	1.0	0.4	0.3
Aliphatic/aromatic products molar ratio	0.22	1.68	0.81	0.30	0.03	0.88	0.30	0.01
Total conversion of anisole (%)	53.4	98.0	82.0	99.0	10.3	99.6	100.0	100.0
HDO degree (%)	30.4	74.7	79.0	81.0	6.3	90.8	94.6	0.5

Table 2
Ni-based catalysts in the anisole hydrodeoxygenation at 300 °C and 1.0 MPa.

Catalyst[a]	Ni/SiO_2	Ni/Cr_2O_3[b]	Ni/Al_2O_3	Ni/ZrO_2	$Ni–Cu/Al_2O_3$	$Ni–Cu/ZrO_2$	$Ni–Cu/CeO_2$[c]
LHSV (h^{-1})	1.0	6.0	1.0	6.0	1.0	0.75	1.0
Aliphatic/aromatic products ratio	1.44	1.53	3.02	0.12	4.81	0.20	–[d]
Total conversion of anisole (%)	92.8	90.2	80.0	26.0	99.6	63.5	100.0
HDO degree (%)	46.0	15.7	95.0	69.0	99.2	60.0	100.0

[a] The probes were taken after 2 h of the anisole hydrodeoxygenation.
[b] One of the tests was run on Ni/Cr_2O_3 (Chirchik, 50 wt.% Ni) to compare the self-synthesized catalysts with the commercial one.
[c] The reaction was carried out at 250 °C because at 300 °C no liquid products formed and 100% conversion to methane was observed.
[d] The only product was cyclohexane.

An additional assumption regarding the choice of the support type was made. Ceria and zirconia were suggested to be the most appropriate materials for the catalyst supports since the valence of these metals can change under the biodiesel HDO conditions. Thus, an additional activation of oxy-organics may be expected.

The presented catalysts were selected for two reasons: to show the effect of copper loading into Ni-based catalysts on their activity and selectivity in the biodiesel HDO reaction, and to determine the influence of the support on the catalyst properties.

The reactions were carried out in a fixed-bed flow reactor under constant reaction conditions, except of temperature. The temperature influence on the efficiency of the tested catalysts is illustrated in Fig. 1.

Fig. 1b shows that in most cases, full conversion of biodiesel is attained in the temperature range of 280–330 °C. The activity of the single $CeO_2–ZrO_2$ was found to be significantly lower compared to the activities of supported Ni and Ni–Cu systems; the biodiesel conversion was about 25%. In addition, this support showed a rapid deactivation due to the coke formation. In the presence of $CeO_2–ZrO_2$, the main reaction product was heptadecane ($C_{17}H_{36}$).

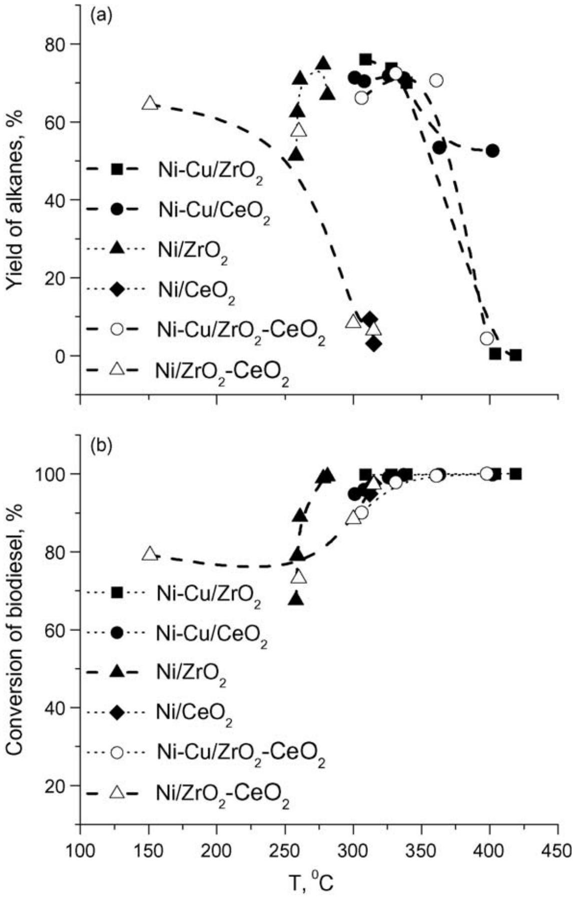


Fig. 1. Biodiesel conversion degrees and alkanes yields (wt.%) vs. reaction temperature under 1.0 MPa of H_2 at LHSV = 2 h^{-1}; the molar ratio of H_2 to the $–CH_2–$ groups in biodiesel is 2.65.

In the case of Ni and Ni–Cu catalysts, the obtained liquid products were linear hydrocarbons $C_6–C_{19}$ and methane in the gas phase. For each catalyst the selectivity towards the heptadecane formation was sufficiently high. The $C_{17}H_{36}$ content in the liquid products was found to be 40–80%. The experiments carried out at different temperatures showed that the heptadecane yield decreases as the temperature rises, whereas the yield of light hydrocarbons becomes higher. It is possible that at higher temperatures, along with hydrogenation and HDO processes, the hydrocracking occurs, leading to the formation of CH_4 and hydrocarbons with a lower molecular weight. Besides, one should not ignore a possible occurrence of decarboxylation reaction with the CO_2 formation, although CO_2 and CO are absent in the gas products of the reaction. Ni-based catalysts are known to be able to perform the carbon oxides methanization under the given reaction conditions [16]. Fig. 1a shows the $C_6–C_{19}$ alkanes yield vs. the reaction temperature. It should be noted that the expected theoretical yield of the oxygen-free products in the biodiesel HDO reaction is about 84 wt.%, while in the case of methyl oleate the reaction path is as follows:

$$\underset{\text{Methyl oleate}}{C_{17}H_{33}COOCH_3} + 5H_2 \rightarrow \underset{\text{Octadecane}}{C_{18}H_{38}} + CH_4 + 2H_2O$$

However, as far as heptadecane was obtained as the main reaction product, it can be concluded that the HDO of FAME involves the decarboxylation (DCO) step, i.e. the removal of carboxyl group, probably followed by methanization of the released CO_2. Heptadecane, formed in the DCO reaction, thereafter undergoes hydrocracking with the light alkanes and methane formation. Analysis of the reaction products indicates that the hydrocarbons chain shortening occurs predominantly by the end $–CH_2–$ groups removal. The temperature rise increases the contribution of hydrocracking process to biodiesel hydrotreatment.

Selectivity of hydrocarbons formation in the biodiesel hydrotreatment is shown in Fig. 2. One can see that the highest selectivity towards the heptadecane formation was attained with the $CeO_2–ZrO_2$ mixed oxide. In the case of the Ni/ZrO_2 catalyst, high content of light hydrocarbons $C_6–C_{12}$ in the reaction products was obtained. The copper addition to this sample leads to the heptadecane formation as a main product. Note that selectivity of the C_{18} and C_{19} hydrocarbons formation was high in the presence of the Ni/CeO_2 catalyst. On this basis one may suggest that the FAMEs deoxygenation occurs via the C–O bonds hydrogenolysis over Ni/CeO_2, while in the presence of the $Ni–Cu/ZrO_2$ sample, HDO proceeds via decarboxylation.

Thus, the total yield of liquid hydrocarbons for biodiesel processing is 75%. When the temperature increases, the yield of liquid products decreases and intensive formation of methane (the undesirable product) starts. From the results of the experiments we can conclude that the temperature required for the biodiesel

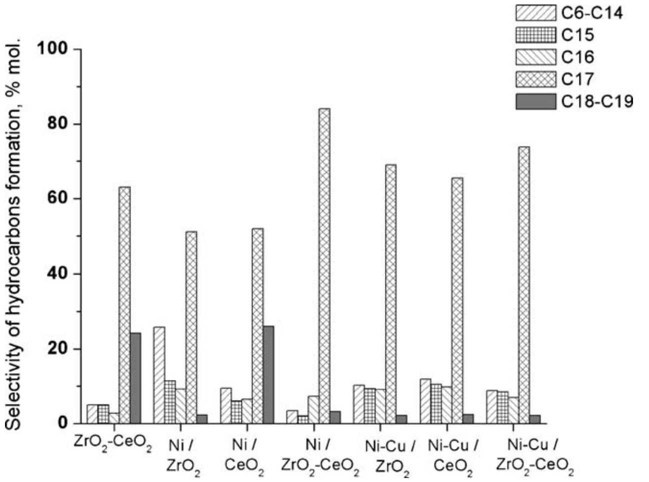


Fig. 2. Selectivity of hydrocarbons formation vs. catalyst type under 1.0 MPa of H_2 at LHSV = 2 h^{-1}; the molar ratio of H_2 to the $-CH_2-$ groups in biodiesel is 2.65.

HDO should be near 340 °C. As far as the HDO and hydrocracking processes are exothermic, one can expect the catalysts layer overheating, which could result in intensification of hydrocracking. This effect may be caused by an uncontrolled temperature rise and, as a result, full methanization of biodiesel. Thus, among the tested catalysts, most attractive are Ni–Cu/CeO_2–ZrO_2 and Ni–Cu/CeO_2 due to their ability to prevent the methane formation over wide temperature range 280–340 °C. In distinction to these catalysts, Ni/CeO_2, Ni/ZrO_2 and Ni/CeO_2–ZrO_2 cannot produce the liquid alkanes in comparable amounts at temperatures above 300 °C. Biodiesel can be almost quantitatively converted to methane over these catalysts even at 320 °C. Fig. 3 shows the methane yields obtained with the above mentioned catalysts.

The lowest biodiesel conversion to methane was obtained using Ni–Cu/CeO_2. Even at so high temperatures as 400 °C, selectivity of the methane formation was quite low. As seen from Fig. 3, single Ni-based catalysts seem to be unpromising for the biodiesel HDO. In the case of Ni/CeO_2, Ni/ZrO_2 and Ni/CeO_2–ZrO_2, at temperatures below 290 °C the biodiesel conversion did not exceed 70%, whereas at 290 °C and higher temperatures the uncontrolled exothermic hydrocracking was observed with full biodiesel conversion to CH_4. Note that even at high temperatures the selectivity towards the light hydrocarbons (C_6–C_{14}) formation in the FAME hydrocracking process is negligible.

To determine the effect of the catalysts composition on their activity in biodiesel HDO, the catalysts were characterized by XRD *in situ* in the oxide and reduced forms. XRD analysis indicated that initial catalysts contain nickel and copper oxides. The *in situ* experiment showed that reduction of Cu-containing catalysts at 300 °C for 3 h leads to the formation of solid solution $Ni_{1-x}Cu_x$ (x = 0.22, . . ., 0.32 depending on the initial loading). In the case of Ni–Cu/CeO_2 (29.9% Cu) catalyst, metallic Cu is also present. The average crystallite sizes of $Ni_{1-x}Cu_x$ are 10–15 nm. The Ni-based catalysts are not fully reduced under these conditions. Increasing the temperature up to 350 °C leads to the formation of metallic nickel.

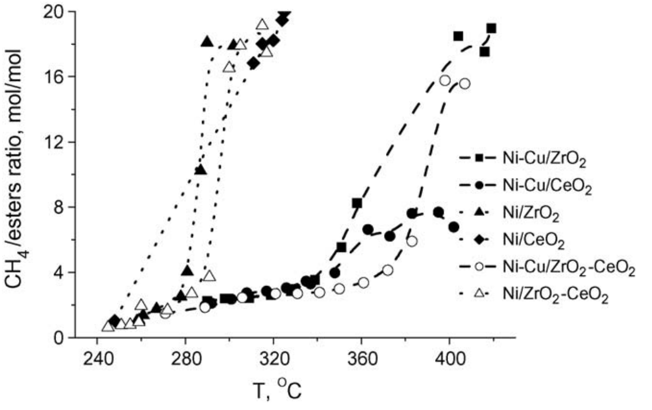


Fig. 3. The molar ratio of the formed CH_4 to the fatty acids methyl esters (biodiesel) vs. temperature under 1.0 MPa of H_2 at LHSV = 2 h^{-1}; the molar ratio of H_2 to the $-CH_2-$ groups in biodiesel is 2.65.

During the reduction, some changes in the XRD pattern of support were observed for Ni–Cu/CeO_2 sample. The CeO_2 lattice parameter increases from 5.417(3) Å to 5.446(2) Å. To determine the nature of the lattice parameter increase we examined behavior of the support during the *in situ* reduction. It was found that the XRD patterns of the initial and reduced supports were identical. In the case of supported Ni, no changes in the lattice parameter are observed.

There are two possible explanations of the effect of the lattice parameter increase during the catalyst reduction. On one hand, Cu may facilitate the support reduction by hydrogen spillover, on the other hand, Cu ions may diffuse into the support structure. Recent studies [17] reveal the formation of anion-defected solid solutions, which can be described by the formula $Cu_xCe_{1-y}O_{2-z\square z}$, where $\square$ is an oxygen vacancy. During the reduction, CuO can be reduced to intermediate Cu_2O. Cuprous oxide Cu_2O, having the primitive cubic lattice and the Cu^{1+} ionic radius equal to 0.115 nm, and CeO_2, having the fluorite structure with the Ce^{4+} ionic radius equal to 0.111, can form at least in theory a substitution solid solution.

4. Conclusions

The performed screening of catalysts demonstrated the possibility of using the supported Ni-based catalysts in the HDO of aliphatic and aromatic oxy-organics. Ni–Cu catalysts were found to be more attractive for the HDO than single Ni catalysts. On one hand, copper facilitates the nickel oxide reduction at temperatures lower than 300 °C. On the other hand, copper prevents methanization of oxy-organics at higher temperatures. The catalyst supports play an important role in hydrotreatment of oxygen-containing compounds. The screening of catalyst supports showed that CeO_2 and ZrO_2 are most effective in the target process, which can be explained by an additional activation of oxy-compounds on the support surface. The prepared catalysts have non-sulfided nature and can be used for upgrading the bioliquids with a low content of sulfur.

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