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Biodiesel Hydrodeoxygenation in the Presence of Catalysts Based on Precious Metals

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Abstract

Catalytic hydrodeoxygenation reaction of biodiesel fuel representing a mixture of fatty acid methyl esters has been studied aiming at obtaining linear alkanes. Precious metals (Ru, Rh, Pd, Ir, Pt), applied onto CeO₂–ZrO₂ binary oxide system were employed as catalysts. It has been demonstrated that these catalysts allow one to deoxygenate efficiently methyl esters of fatty acids at hydrogen pressure of 0.5 MPa within a wide temperature range (300–380 °C) with obtaining mainly heptadecane (C₁₇H₃₆). However, only in the presence of Rh and Ru catalysts the yield of alkanes is quantitative. The process of obtaining linear alkanes of C₁₄–C₁₈ series via this method is positioned as a stage of producing high-quality phylogenous kerosene fuel.

Key words: catalyst, hydrodeoxygenation, biodiesel fuel, biofuel, methyl esters of fatty acids

INTRODUCTION

Biodiesel fuel, alongside with bioethanol, at the present time represents the most widespread kind of phylogenous biofuel and is positioned as the improving additive to traditional motor топливам. The biodiesel fuel represents a mixture of the saturated and unsaturated methyl esters of fatty acids of C₁₈–C₂₀ series. The fractional composition of biodiesel fuel obtained from rapeseed oil is presented in Table 1.

Recently a number of papers have been published devoted to hydrodeoxygenation of fatty acid esters, the compounds simulating biodiesel fuel [1]. These studies have been initiated by the necessity for improving the characteristics of biodiesel fuel as motor fuel in order to obtain biofuel of the second generation, so-called green diesel [2]. It should be noted that traditional desulphurization catalysts such as sulphided Co–Mo and Ni–Mo catalysts were

used for hydrodeoxygenation of methyl esters of fatty acids [2, 4]. These catalysts also demonstrate a certain activity in the reactions of deoxygenation [5]. However, in order to maintain the catalyst in active condition the initial mixture should be added with organosulphur compounds such as H₂S, thiophene [6]. A typical route for the hydrodeoxygenation of esters of fatty acids includes the hydrogenation of double bonds, decarboxylation with the removal of ester groups and hydrocracking with the obtaining of light hydrocarbons.

The present work is devoted to the studies on the possibility for using precious metals of non-sulphide nature as catalysts for efficient deoxygenation of methyl esters of fatty acids composing biodiesel fuel, to produce corresponding alkanes. As a carrier for catalysts, we have chosen mixed ZrO₂–CeO₂ oxide prepared employing the method of co-precipitation [7]. The choice of the carrier is based on the assump-

TABLE 1

Physical parameters of biodiesel fuel and its components

Substrates	Molar fraction, %	<i>M</i> , g/mol	ρ , g/mL	M. p., °C	B. p., °C
Biodiesel fuel		297.7	0.88	no data	216
Methyl ester of oleic acid $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$	59	296.5	0.88	-19	217
Methyl ester of linoleic acids $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$	20	294.5	0.89	-15.4	211
Methyl ester of stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$	10	298.5	0.86	38	215
Methyl ester of linolenic acid $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$	8	292.4	0.90	43	231
Methyl ester of erucic acid $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOCH}_3$	3	352.6	0.81	31	281

tion that the mixed $\text{ZiO}_2\text{-CeO}_2$ oxide has active centres with mobile oxygen whereon an additional activation of oxygen-containing organic compounds would be realized.

EXPERIMENTAL

The catalysts were synthesized employing the method of impregnating a mixed $\text{ZiO}_2\text{-CeO}_2$ oxide using the solutions of acids with corresponding VIII group metals; the mixed oxide having the following characteristics: $A_{\text{BET}} = 141.62 \text{ m}^2/\text{g}$, $V_{\text{por}} = 0.095 \text{ cm}^3/\text{g}$, $\langle d \rangle = 2.69 \text{ nm}$ [7]. The samples impregnated were dried at 120°C during 24 h and then they were calcinated at 450°C for 2 h. The content of a noble metal in the catalyst was determined employing an elemental analysis technique.

The testing of catalysts was performed within a reactor with a fixed-bed catalyst layer at the temperature of $290\text{--}300^\circ\text{C}$ and at the pressure of 1.0 MPa. To the catalyst of 1.5 mL in volume (the grain size of 0.2–0.5 mm) was added 0.5 mL of quartz sand with the same grain size and loaded this into the reactor. The volume flow rate of gases under feeding (H_2 and Ar) amounted to 10 L/h. The biodiesel fuel was fed into the reactor with the flow rate of 3 mL/h, *i. e.* the load on the catalyst (LHSV) amounted to 2 h^{-1} . After the processing in the reactor, a part of products was condensed within a trap

thermostated at 50°C . Further they were taken for chromatographic analysis performed employing a Chromos GC 1000 chromatograph with the help of a Zebron ZB-5 capillary column (the stationary phase being 5% phenylpolysiloxane and 95% dimethylpolysiloxane, 30 m long, with the internal diameter of 0.32 mm, phase thickness of 0.25 mm). The analysis of the gas phase (H_2 , CO, CO_2 , CH_4) was carried out in an online mode employing a Chromos GC 1000 chromatograph with the help of packed columns with Silochrom (3 m in length, internal diameter being of 2 mm) with detectors such as TCD and FID.

The investigation of catalysts was also carried out using a method temperature-programmed reduction (TPR) in the flow of H_2 (10%) and Ar (90%) gas mixture, the flow rate being of 40 mL/min, the mass of the weighed portion of the catalyst being equal to 0.2 g. Samples were placed in a U-shaped quartz reactor and then were heated in a reducing atmosphere with a constant rate of heating ($5^\circ\text{C}/\text{min}$) up to the temperature of 700°C being reached. The variation of hydrogen concentration in the mixture at the reactor outlet was registered by means of a thermal conductivity detector (TCD).

The measurements of the textural characteristics of samples were performed basing on N_2 physical adsorption at the temperature of liquid nitrogen with the use ASAP-2400 auto-

TABLE 2

Textural characteristics of catalysts M/ZrO₂-CeO₂ (M = Pt, Pd, Rh, Ru, Ir)

Catalysts	A_{BET} , m ² /g	V_{por} , cm ³ /g	$\langle d \rangle$, nm
Pt/ZrO ₂ -CeO ₂	114	0.08	2.6
Pd/ZrO ₂ -CeO ₂	113	0.08	2.6
Rh/ZrO ₂ -CeO ₂	112	0.07	2.7
Ru/ZrO ₂ -CeO ₂	113	0.07	2.6
Ir/ZrO ₂ -CeO ₂	110	0.08	2.7
ZrO ₂ -CeO ₂	142	0.095	2.7

matic volumetric adsorption device (Micromeritics Instrument Corp., Norcross, GA, USA). Before the analysis, the samples under investigation were calcinated at the temperature of 150 °C during 4 h at a pressure of 10⁻³ mm Hg. The duration of the analysis was varied depending on a particular sample. The adsorption isotherms obtained used for the calculation of the specific surface A_{BET} , total pore volume V_{por} (according to the limiting saturation at a relative pressure $P/P_0 = 1$), the volume of micropores V and the surface A_{ext} remaining after filling the pores (Table 2).

The studies on the chosen samples using the method of high resolution electron microscopy (TEM) were carried out employing JEM-2010 transmission electron microscope (JEOL, Japan) with the accelerating voltage of 200 kV and the resolution of 0.14 nm.

RESULTS AND DISCUSSION

Studying the products of biodiesel fuel hydrodeoxygenation

Aiming at determining the most active component in the reaction of hydrodeoxygenation, a series of impregnated catalysts has been prepared with the identical content of precious metals on the surface of ZrO₂-CeO₂. For determining the optimum conditions of target reaction we have plotted the conversion level of biodiesel fuel (a mixture of methyl esters of fatty acids) against the temperature (Fig. 1).

One can see that precious metals demonstrate various activities in the target process. The greatest activity within the temperature range under investigation is inherent in Rh/ZrO₂-CeO₂

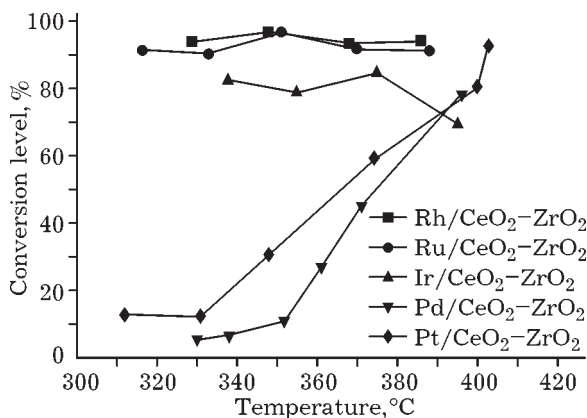


Fig. 1. Biodiesel fuel conversion level depending on the temperature in the course of biodiesel fuel hydrodeoxygenation in the presence of catalysts based on precious metals. Hydrogen pressure being of 1 MPa, LHSV = 2 h⁻¹.

and Ru/ZrO₂-CeO₂ catalysts. In the case of employing Pd/ZrO₂-CeO₂ and Pt/ZrO₂-CeO₂ the conversion level of biodiesel fuel increases with the increase in the temperature.

Figure 2 demonstrates the yield of target products such as alkanes depending on the reaction temperature. One can see that the character of alkane yield temperature dependence as a whole is similar to the character the temperature dependence inherent in the biodiesel fuel conversion level. The main product of biodiesel fuel deoxygenation (with the content of the methyl esters of C₁₈ series carboxylic acids amounting to 97 %) represents heptadecane C₁₇H₃₆. In this case the yield of liquid hydrocarbons should not exceed 80 mass %. In the case of Rh and Ru catalysts one can observe

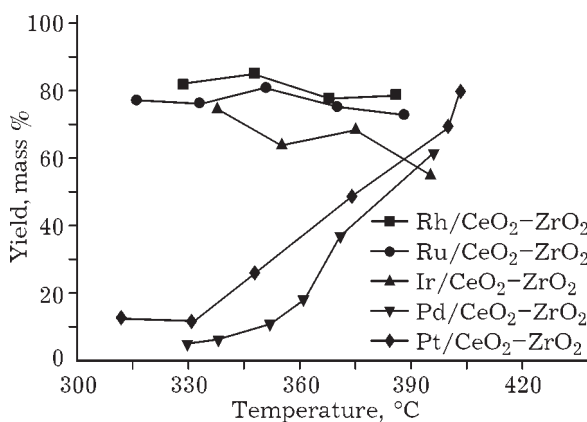


Fig. 2. Yield of alkanes depending on the temperature in the course of biodiesel fuel hydrodeoxygenation in the presence of catalysts based on precious metals. Hydrogen pressure being of 1 MPa, LHSV = 2 h⁻¹.

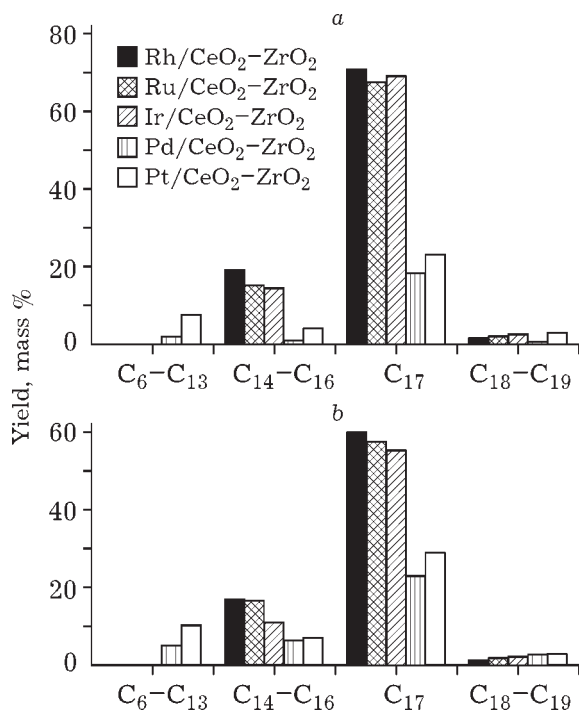


Fig. 3. Alkane yield distribution throughout the fractions for each type of catalyst in the course of biodiesel fuel hydrodeoxygenation at the temperature of 330 (a) and 370 °C (b). Hydrogen pressure being of 1 MPa, LHSV = 2 h⁻¹.

an almost quantitative formation of the target products such as alkanes.

It should be noted that the distribution character of alkanes for each type of catalysts almost does not depend on the temperature of the process. Figure 3 displays the curves characterizing the distribution of alkane yield for each type of catalyst at 330 and 370 °C. One can see that at both temperatures of the process the main product of deoxygenation is presented by heptadecane. The yield of C₁₄-C₁₆ fraction does not exceed 20 mass % of the initial biodiesel fuel within entire temperature range under investigation. A much deeper cracking of fatty acid residues of biodiesel fuel with the formation of more light hydrocarbons of C₆-C₁₃ series is observed only in the presence of Pd and Pt catalysts, and the total yield of C₆-C₁₃ hydrocarbons does not exceed 10 mass %. Thus, for obtaining biofuel intended for the application in diesel engines, it is preferable to use Rh, Ru or Ir catalysts.

It should be noted as well, that there is methane formation as a by-product observed under the hydrodeoxygenation of methyl es-

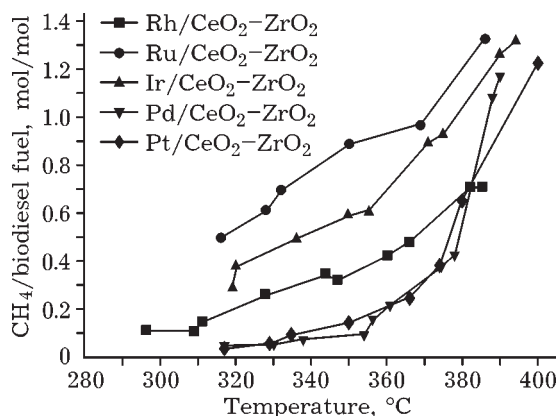
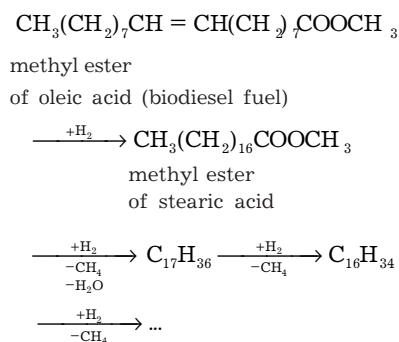


Fig. 4. Molar ratio CH₄/biodiesel fuel depending on the process temperature for biodiesel fuel hydrodeoxygenation. Hydrogen pressure being of 1 MPa, LHSV = 2 h⁻¹, the average molecular mass of biodiesel fuel amounting to 297.7 g/mol.

ters. It is connected with the course of undesirable processes those result in the increase in hydrogen consumption of and the decrease of the yield of liquid hydrocarbons. Figure 4 displays the molar CH₄/biodiesel ratio depending on the biodiesel fuel hydrodeoxygenation temperature in the presence of catalysts under testing. One can see that formation of methane as a whole does not exceed 1 mol/mol of carboxylic acid methyl ester. To all appearance, the methyl surface groups formed on the surface of an active component in the process of hydrodeoxygenation of fatty acid methyl esters are capable of migration with the formation of methane and more high-molecular hydrocarbons.

Basing on the experimental data obtained, by the example of oleic acid methyl ester we have proposed a reaction scheme for the hydrodeoxygenation of fatty acids esters (Scheme 1). At the first stage, the hydrogenation occurs concerning the double bonds of fatty acid residues of methyl esters to result in the formation of mainly the ester of stearic acid. The main product at the stage of deoxygenation represents heptadecane, therefore at the second stage the reaction of the ester group decarboxylation could be proposed with the subsequent hydrogenation of the carboxylic fragment (see Scheme 1). As the result of the second stage, linear alkanes are formed (mainly heptadecane), methane and water. Much lighter hydrocarbons are formed at the subsequent stages of hydrocracking. It should be noted that hydrocarbons lighter than tridecane (C₁₃) are



Scheme 1. Hydrodeoxygenation of fatty acid esters.

not formed under the given reaction conditions in the presence of the catalysts under investigation. The yield of tridecane and tetradecane is insignificant, which indicates a high selectivity of catalysts under testing with respect to the process of deoxygenation.

Studies on catalysts for the hydrodeoxygenation of biodiesel fuel

In order to characterize the properties of catalysts for the hydrodeoxygenation fatty acid methyl esters we used a TPR method which allows researchers not only to determine the temperature of the reduction of the oxidized forms of a catalyst, but also to estimate the amount of hydrogen absorbed. Figure 5 demonstrates the TPR curves for catalysts under investigation and $\text{CeO}_2\text{-ZrO}_2$ carrier.

One can see that for each catalyst the profiles of TPR exhibit two characteristic temperature regions of hydrogen absorption: the main peak at 150–250 °C and a wide weak peak at 300–500 °C. It is obvious, that at the temperature values of 150–250 °C, the reduction of precious metal oxides occurs to produce the metallic state. A high-temperature region of hydrogen absorption (300–500 °C), to all appearance, corresponds to the partial reduction of the carrier surface.

Table 3 demonstrates data concerning the amount of absorbed hydrogen within the temperature regions under consideration. One can see that in the presence of catalysts (except for a Pt-containing sample) the amount of hydrogen absorbed within a low-temperature region is higher as compared to that for high-temperature region. For each catalyst, we have

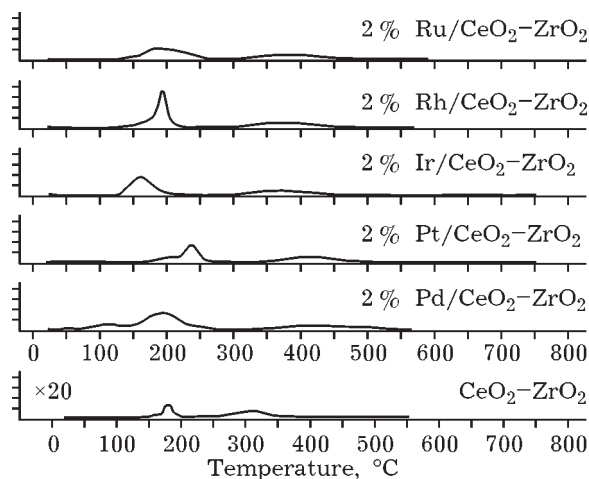


Fig. 5. TPR profile for hydrodeoxygenation catalysts and $\text{CeO}_2\text{-ZrO}_2$ carrier.

determined the amount of H_2 necessary for the reduction of corresponding amount of precious metal oxide contained in the sample. It is seen that the calculated data concerning the amount of hydrogen are much less as compared to the data concerning the total amount of hydrogen absorbed within the range of 100–250 °C. This fact could be caused both by hydrogen dissolution in the bulk phase of a precious metal, and by hydrogen spillover (moving) from the phase of a precious metal to the surface of the oxide carrier. A considerable absorption of hydrogen at 300–500 °C should be attributed to a partial reduction of the surface of the oxide carrier.

Figure 6 demonstrates an electron microscopy picture and high-resolution spectrum of 2% Rh/ $\text{CeO}_2\text{-ZrO}_2$ sample. According to electron microscopy data, the carrier of the cata-

TABLE 3

Data on the amount of absorbed hydrogen within temperature range under investigation

Catalysts	Amount of the absorbed hydrogen per 1 g of sample (mmol) at a temperature, °C	
	100–250	300–500
2% Ru/ $\text{CeO}_2\text{-ZrO}_2$	0.97 (0.297)	0.73
2% Rh/ $\text{CeO}_2\text{-ZrO}_2$	0.96 (0.389)	0.68
2% Ir/ $\text{CeO}_2\text{-ZrO}_2$	0.82 (0.156)	0.695
2% Pt/ $\text{CeO}_2\text{-ZrO}_2$	0.71 (0.205)	0.71
2% Pd/ $\text{CeO}_2\text{-ZrO}_2$	1.56 (0.188)	0.98

Note. In parenthesis there are calculated data concerning the amount of hydrogen necessary for the reduction of precious metal oxide contained in a sample.

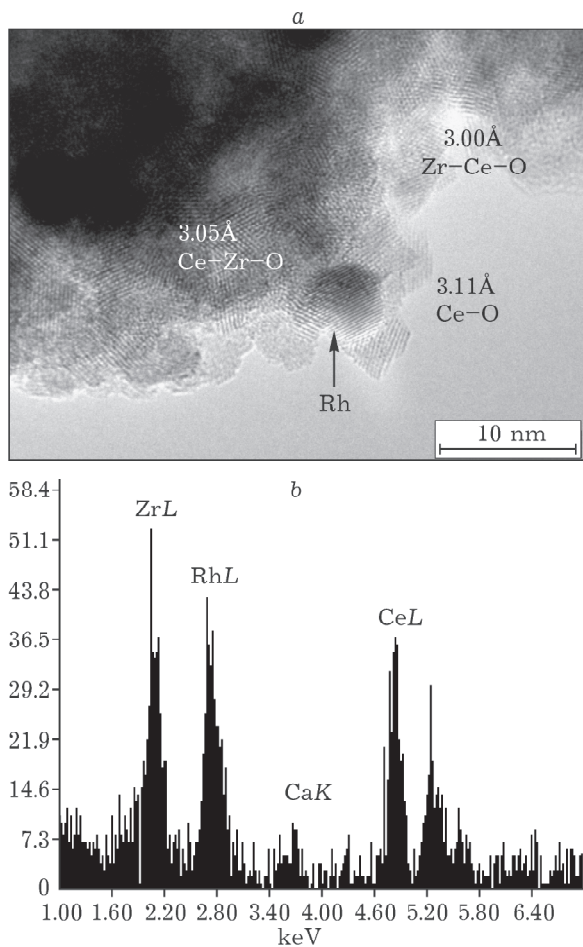


Fig. 6. TEM images and high resolution spectrum of 2% Rh/CeO₂-ZrO₂ sample.

lyst consists of disordered crystallites with variable composition of 5–7 nm in size. Depending on CeO₂-ZrO₂ ratio, the interplane distance within the crystal lattice of the bimetallic phase ranges from 2.9 to 3.1 Å. Rhodium is located on the surface of the carrier in the form of particles of 1–5 nm in size. The effects observed

for the rhodium catalyst are inherent in all the catalysts under investigation.

CONCLUSION

It has been demonstrated that the catalysts employed exhibit significant activity in the process of the hydrodeoxygenation of fatty acid methyl esters. As far as the textural characteristics are concerned, as well the ability of activating hydrogen, the catalysts under investigation based on precious metals exhibit similar properties. However, the catalysts under investigation exhibit different activity in the target reaction. To all appearance, the efficiency of the process is influenced mainly by the nature of a precious metal. It has been demonstrated that in the series of precious metals under consideration, the greatest activity is exhibited by Rh- and Ru-catalysts. The process of obtaining linear alkanes of C₁₄-C₁₈ series via the method suggested is positioned as a process of producing high-quality kerosene fuel.

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