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Hydrodeoxygenation of Palmitic and Stearic Acids on Phosphide Catalysts Obtained in situ in Reaction Medium

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Abstract—Unsupported phosphide catalysts of composition Ni_2P and CoP are prepared in situ in the reaction medium from oil-soluble precursors in the course of hydrodeoxygenation of palmitic and stearic acids. The obtained catalysts are characterized by X-ray powder diffraction and X-ray photoelectron spectroscopy; they show high activity in the hydrodeoxygenation of model substrates. After 6 h of the hydrodeoxygenation reactions, the conversion of palmitic acid reaches 93 and 92% and the conversion of stearic acid is as high as 94 and 91% in the presence of nickel phosphide and cobalt phosphide, respectively. It is shown that the catalyst formed in situ can be isolated and recycled.

Keywords: hydrodeoxygenation, vegetable oils, green diesel, transition metal phosphides, Ni_2P, CoP
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Over the past decade and a half, the number of studies addressing the production of fuels from biomass and their conversions has increased significantly. One of the promising types of biofuels is biodiesel. Vegetable oils and animal fats are the source for its production. The generally accepted method for producing biodiesel is acid-catalyzed transesterification, which results in methyl esters and glycerol formed from fatty acid triglycerides [1]. An attractive method for manufacturing environmentally friendly diesel fuel is the catalytic hydrodeoxygenation of vegetable oils in order to produce saturated hydrocarbons. The fuel obtained by this technology is patented under the name Green Diesel.[1] In contrast to fatty acid methyl esters, Green Diesel can be used not only as an additive to motor fuels produced from fossil sources but also as an independent fuel [2].

The removal of oxygen from fatty acids can be realized in three ways, including hydrodeoxygenation (HDO), decarbonylation (DCO), and decarboxylation (DCO_2) [3, 4].

$$\begin{aligned} \mathrm{RCOOH} + 3\mathrm{H_2} &\rightarrow \mathrm{RCH_3} + 2\mathrm{H_2} \quad (\mathrm{HDO}),\\ \mathrm{RCOOH} + \mathrm{H_2} &\rightarrow \mathrm{RH} + \mathrm{CO} + \mathrm{H_2O} \quad (\mathrm{DCO}),\\ \mathrm{RCOOH} &\rightarrow \mathrm{RH} + \mathrm{CO_2} \quad (\mathrm{DCO_2}). \end{aligned}$$

According to hydrogen consumption, these reactions can be arranged in the following order: HDO > DCO > DCO_2 [5, 6]. Thus, if the reaction proceeds along the decarboxylation pathway, the consumption of hydrogen is not required and the reaction will proceed in an inert atmosphere. Aldehydes, alcohols, and olefins can be formed in the system as intermediate products [7].

Most of hydrodeoxygenation catalysts are oxide-supported noble metals and transition metal sulfides. The noble metals are highly active in the hydrodeoxygenation of both fatty acids themselves and their methyl esters; however, catalysts based on them have a high cost. Transition metal sulfides seem to be economically attractive; however, oxygen contained in the feed reduces their catalytic activity; therefore, additional sulfidation is required [8]. Transition metal phosphides are an interesting alternative for use in hydrodeoxygenation reactions. They remove oxygen well from substrates, are fairly stable, and are less expensive than catalysts based on transition metal sulfides [9].

The hydrodeoxygenation of fatty acids and their methyl esters on phosphide catalysts was previously described in a number of studies, for example [3, 5, 7, 9]. Transformations proceeded with a high conversion, and RCH_3 and RH saturated hydrocarbons were formed as key products from RCOOH acids or their methyl esters $RCOOCH_3$.

In this work, the hydrodeoxygenation of palmitic and stearic acids was studied in the presence of nickel and cobalt oil-soluble salts and trioctylphosphine. The aim of this work was to obtain nickel and cobalt

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[1] https://www.uop.com/processing-solutions/renewables/green-diesel.

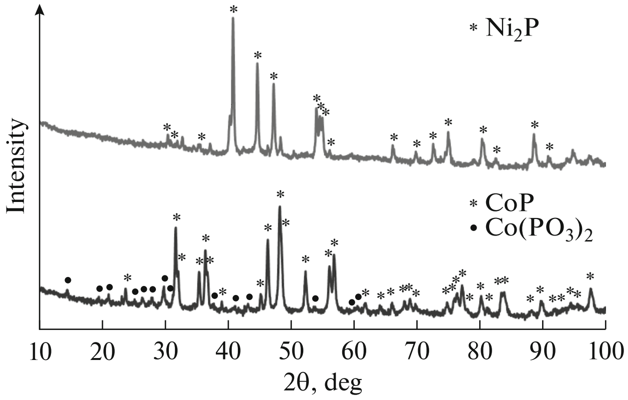

Fig. 1. X-ray powder diffraction patterns of nickel and cobalt phosphides formed in situ from oil-soluble precursors in the reaction medium. Phases identified: Ni_2P (PDF#65-9706), CoP (PDF#29-0497), and $Co(PO_3)_2$ (PDF#27-1120).

phosphides in situ in the reaction medium and to examine their catalytic activity.

EXPERIMENTAL

Materials. The catalysts were prepared using cobalt(II) 2-ethyl hexanoate (Aldrich, 65 wt % solution in C_{10}–C_{13} *iso*-alkanes), nickel(II) 2-ethyl hexanoate (Aldrich, 78 wt % solution in 2-ethylhexanoic acid), and trioctylphosphine (Acros, 90%). Stearic acid (Komponent reaktiv, Russia; high-purity grade) and palmitic acid (Reakhim, Russia; high-purity grade) were used as substrates, and benzene (Ekros, Russia; reagent grade) was used as a solvent. H_2 (Air Liquide, ≥98%) and Ar (Air Liquide, ≥98%) gases were used. In addition, methanol (Reakhim, reagent grade), acetyl chloride (Sigma-Aldrich, ≥99%), *n*-heptane (Komponent reaktiv, reagent grade), ethanol (Reakhim, reagent grade), $KMnO_4$ (Komponent reaktiv, high-purity grade), and K_2CO_3 (Komponent reaktiv, high-purity grade) were used. All solvents were purified by standard procedures.

Catalyst synthesis and catalytic activity runs. The calculated amount of precursors (0.0436 mmol of cobalt(II) or nickel(II) 2-ethyl hexanoate and 0.0872 mmol of trioctylphosphine, respectively), substrate (0.218 mmol of stearic or palmitic acid), solvent (3 g of benzene), and a magnetic stirrer were placed in a 45-cm^3 stainless steel autoclave. The autoclave was pressurized, filled with hydrogen to a pressure of 5 MPa, and placed in an oven. The reaction was carried out under vigorous stirring at 350°C for 3 and 6 h. Temperature was controlled using a thermocouple. Upon completion of the reaction, the autoclave was cooled and the gas was passed through a $KMnO_4$ solution. Afterwards, the autoclave was depressurized. The reaction products were separated from the resulting catalyst via centrifugation and analyzed by gas chromatography methods using a flame ionization detector (GC-FID) and a mass spectrometric detector (GC-MS). The catalyst was washed with *n*-hexane and ethanol and dried in a fume hood. After that, the catalyst was analyzed by X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Instruments and methods. The qualitative analysis of liquid products was carried out on a Finnigan MAT 95 XL gas-liquid chromatograph (Thermo Scientific) equipped with a mass spectrometric detector and a Varian VF-5MS capillary column (30 m × 0.25 mm × 0.25 μm) using helium as a carrier gas. The quantitative analysis of liquid products was carried out on a Kristallyuks 4000M gas-liquid chromatograph (Meta-Chrom) equipped with a flame ionization detector and an SPB-1 capillary column (Superlco, 30 m × 0.25 mm × 0.25 μm) using helium as a carrier gas. Before quantitative analysis, samples were prepared according to the known procedure [10]. The sample solution (1 mL) was placed in a vial, and methanol (1 mL) was added. Acetyl chloride (50 μL) was carefully added dropwise to the mixture. The resulting mixture was held under stirring for 2 h at a temperature of 70°C until methyl esters of fatty acids formed. The mixture was cooled to room temperature, and benzene (2 mL) was added. The pH of the reaction mixture was neutralized with an aqueous K_2CO_3 solution. Then the resulting mixture was shaken and centrifuged for 5 min (5000 rpm). The nonpolar phase was analyzed.

The XRD analysis of the catalysts was carried out using a Rotaflex RU-200 (Rigaku) diffractometer (CuK_α radiation) in the 2θ angle range of 5°–100° with a D/Max-RC (Rigaku) goniometer at a rotation speed of 1° 2θ/min with a step of 0.04°. The average crystallite size was estimated from the widths of corresponding reflections using the Scherrer formula (Fig. 1).

The XPS analysis of the catalysts was carried out on an ESCALAB MK2 electron spectrometer (Vacuum Generators Ltd.). The surface of the samples was investigated without heating and ion-beam treatment; the position of the lines of elements was normalized to the position of the carbon line C1*s* due to hydrocarbon surface contamination. The survey spectrum was obtained at an analyzer pass band of 50 eV with a scan step of 0.25 eV; partial element spectra were obtained at a pass band of 20 eV with a scan step of 0.2 eV.

RESULTS AND DISCUSSION

In the nickel phosphide sample, the crystalline phase of the phosphide of composition Ni_2P (PDF#65-9706) was identified; the average crystallite size was 50 nm. Two crystalline phases were identified in the cobalt phosphide sample: the phosphide phase of composition CoP (PDF#29-0497) and the cobalt metaphosphate phase $Co(PO_3)_2$ (PDF#27-1120). The average crystallite size of the phases was 52 and 23 nm,

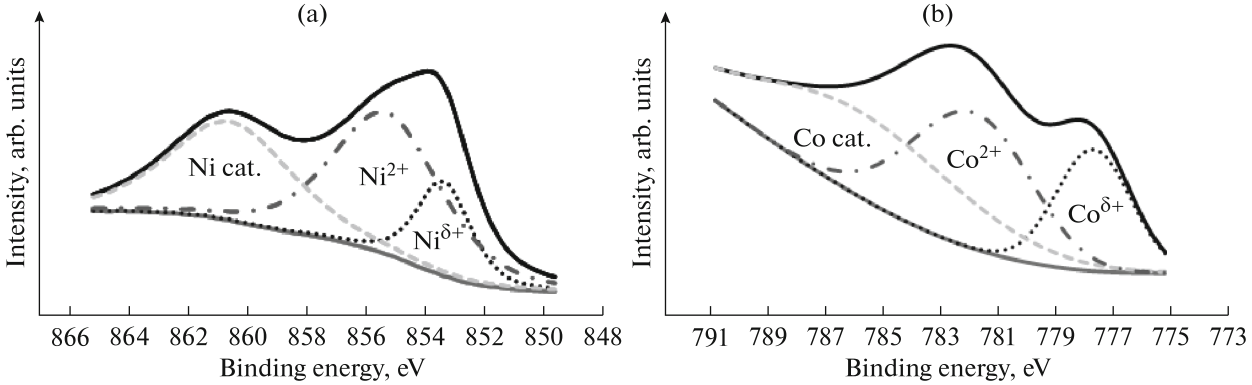

Fig. 2. XPS spectra for the region: (a) Ni $2p_{3/2}$ and (b) Co $2p_{3/2}$.

respectively. Formation of the cobalt metaphosphate phase could result from interaction between the obtained phosphide and atmospheric oxygen [11].

The chemical states of phosphorus, nickel, and cobalt on the surface of phosphides obtained in situ were characterized by XPS. A binding energy of 853.4 eV corresponds to $Ni^{\delta+}$ in Ni_2P and is close in magnitude to that of Ni^0 in metallic nickel (Fig. 2a) [12]. Binding energies of 855.4 and 860.8 eV refer to nickel in the oxidized state which can be associated with nickel phosphate and satellite of the Ni $2p_{3/2}$ peak, respectively [12]. For the cobalt phosphide sample, binding energies of 777.8, 782.2, and 786.0 eV correspond to $Co^{\delta+}$ in CoP, oxidized Co, and satellite of the Co $2p_{3/2}$ peak, respectively (Fig. 2b) [13].

The catalytic activity of nickel and cobalt phosphides formed in situ was studied (Tables 1, 2). For both catalytic systems, conversions and selectivities in the hydrodeoxygenation of fatty acids were found to be comparable. When palmitic acid hydrodeoxygenation was carried out for 6 h in the presence of nickel phosphide and cobalt phosphide, conversion reached 93 and 92%, respectively. The conversion of stearic acid in the presence of nickel phosphide and cobalt phosphide after 6 h was as high as 94 and 91%, respectively. For the system containing cobalt phosphide the fatty acid conversion was lower than for the system containing nickel phosphide after reaction over both 3 and 6 h. However, with the system containing nickel phosphide, a greater amount of alcohol was formed compared with the system containing cobalt phosphide. Thus, the degree of removal of oxygen in the presence of the cobalt catalyst was higher than that in the presence of the nickel catalyst. Ratio RCH_3/RH varied around unity; therefore, after reaction for 3 h it was slightly lower than one, while after reaction for 6 h it was slightly above one; that is, reactions of all three types occur in the system, namely, HDO, DCO, and DCO_2, with HDO being predominant.

The same dependence was previously observed in [7, 14]. Among the reaction products, *n*-alkanes with a smaller number of C atoms were also identified; this fact indicates the occurrence of cracking in the system. Aldehydes and olefins were not found among the products. Not only the hydrogenation of unsaturated bonds, but also the occurrence of oxygen removal reactions on unsupported transition metal phosphides indicates the presence of acid sites in such catalysts. The presence of Lewis sites in nickel phosphide catalysts, which arise due to the transfer of electrons from metal to phosphorus, was reported in [15, 16]. In addition, all unreduced PO_x groups located on the surface of the phosphide catalyst are characterized by the presence of Brønsted acid sites [17, 18], which are reduced at temperatures above 400°C [19].

The activities of nickel and cobalt phosphides in the hydrodeoxygenation of vegetable oils were com-

Table 1. Results of palmitic acid (C_{16}) catalytic conversions in the presence of various catalysts (350°C; H_2, 5 MPa; *n*-C_{15}—pentadecane; *n*-C_{16}—hexadecane; *n*-$C_{16}OH$—hexadecanol; *n*-C_{10}—C_{14}—*n*-alkanes C_{10}—C_{14})

Catalyst, reaction time	Palmitic acid conversion, %	Selectivity (%) for				*n*-C_{16}/*n*-C_{15}, mol/mol
		n-C_{15}	*n*-C_{16}	*n*-$C_{16}OH$	*n*-C_{10}—C_{14}	
Ni_2P, 3 h	86	38	29	28	5	0.76
Ni_2P, 6 h	93	39	46	9	6	1.18
CoP, 3 h	81	46	31	21	2	0.67
CoP, 6 h	92	42	48	3	7	1.14

Table 2. Results of stearic acid (C_{18}) catalytic conversion in the presence of various catalysts (350°C; H_2, 5 MPa; n-C_{17}—heptadecane; n-C_{18}—octadecane; n-$C_{18}OH$—octadecanol; n-C_{12}–C_{16}—n-alkanes C_{12}–C_{16})

Catalyst, reaction time	Stearic acid conversion, %	Selectivity (%) for				n-C_{18}/n-C_{17}, mol/mol
		n-C_{17}	n-C_{18}	n-$C_{18}OH$	n-C_{12}–C_{16}	
Ni_2P, 3 h	86	41	31	24	4	0.76
Ni_2P, 6 h	94	42	46	7	5	1.10
CoP, 3 h	77	47	32	18	3	0.68
CoP, 6 h	91	45	48	3	4	1.07

pared in [9, 20]. Methyl laurate was used as a substrate. In [9], phosphides were obtained by reducing a phosphite precursor, while in [20] they were prepared by reducing a phosphate precursor. According to X-ray powder diffraction, in both cases, the catalyst based on nickel phosphide contained one Ni_2P phosphide phase; two phases CoP and Co_2P were identified in the cobalt phosphide catalyst. In this case, conversion reached 71.9 and 77.6% [9] and 95.9 and 45.8% [20] in the presence of Ni and Co catalysts, respectively. The n-C_{12}/n-C_{11} ratio varied from 0.16 to 0.24. According to these data, it can be inferred that DCO and DCO_2 reactions prevailed in these systems.

In this study, tests also included the isolation of the phosphides obtained in situ in the reaction medium and the recycling of catalysts (Fig. 3). The activity of the isolated cobalt and nickel phosphides in palmitic acid hydrotransformations differed insignificantly from the activity of the catalysts obtained in situ.

Thus, in this study, phosphides were prepared in situ from nickel or cobalt 2-ethyl hexanoate and trioctylphosphine in the reaction medium during the reactions of oxygen removal from fatty acids. It is shown that using these precursors with P : M = 2 phosphides of the composition Ni_2P and CoP can be obtained. The results of catalytic tests make it possible to state that nickel phosphide and cobalt phosphide are equally active in oxygen removal reactions and they both catalyze the HDO reactions as well as the DCO and DCO_2 reactions. When the catalyst isolated was recycled, its activity was almost the same as that of the system in which the catalyst was formed in situ; therefore, it can be concluded that nickel and cobalt phosphides formed in the system make the main contribution to the hydrodeoxygenation of fatty acids.

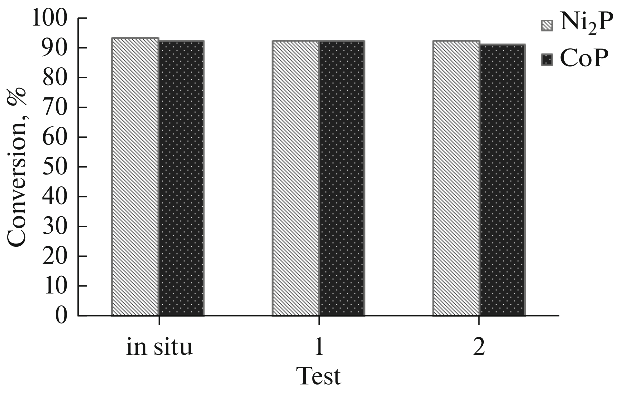

Fig. 3. Comparison of palmitic acid conversion on phosphides formed in situ and catalysts isolated over two cycles.

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CONFLICT OF INTEREST

A.L. Maximov is the editor-in-chief of the journal *Petroleum Chemistry*; M.A. Golubeva declares that there is no conflict of interest.

ADDITIONAL INFORMATION

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