HDO of Methyl Palmitate over Silica-Supported Ni Phosphides: Insight into Ni/P Effect

Irina V. Deliy * , Ivan V. Shamanaev , Evgeny Yu. Gerasimov , Vera P. Pakharukova, Ilya V. Yakovlev, Olga B. Lapina, Pavel V. Aleksandrov and Galina A. Bukhtiyarova

Bioreskov Institute of Catalysis, Pr. Lavrentieva 5, 630090 Novosibirsk, Russia; i.v.shamanaev@catalysis.ru (I.V.S.); gerasimov@catalysis.ru (E.Y.G.); verapakharukova@yandex.ru (V.P.P.); spitzstichel@gmail.com (I.V.Y.); olga@catalysis.ru (O.B.L); aleksandrov@catalysis.ru (P.V.A.); gab@catalysis.ru (G.A.B.)

* Correspondence: delij@catalysis.ru; Tel.: +7-383-326-9410

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Abstract: Two sets of silica-supported nickel phosphide catalysts with a nickel content of about 2.5 and 10 wt % and Ni/P molar ratio 2/1, 1/1 and 1/2 in each set, were prepared by way of a temperature-programmed reduction method using (Ni(CH\textsubscript{3}COO)	extsubscript{2}) and ((NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4}) as a precursor. The Ni\textsubscript{x}P\textsubscript{y}/SiO\textsubscript{2} catalysts were characterized using chemical analysis N\textsubscript{2} physisorption, XRD, TEM, \textsuperscript{31}P MAS NMR. Methyl palmitate hydrodeoxygenation (HDO) was performed in a trickle-bed reactor at 3 MPa and 290 °C with LHSV ranging from 0.3 to 16 h\textsuperscript{-1}. The Ni/P ratio was found to affect the nickel phosphide phase composition, PO\textsubscript{x} groups content and catalytic properties in methyl palmitate HDO with the TOF increased along with a decline of Ni/P ratio and a growth of PO\textsubscript{x} groups’ content. Taking into account the possible routes of methyl palmitate conversion (metal-catalyzed hydrogenolysis or acid-catalyzed hydrolysis), we proposed that the enhancement of acid PO\textsubscript{x} groups’ content with the Ni/P ratio decrease provides an enhancement of the rate of methyl palmitate conversion through the acceleration of acid-catalyzed hydrolysis.

Keywords: nickel phosphide; Ni/P ratio; nickel content; PO\textsubscript{x} groups content; \textsuperscript{31}P MAS NMR; acidity; hydrodeoxygenation; methyl palmitate

1. Introduction

Triglyceride-based feedstocks are widely studied as a resource for the production of diesel-range or aviation fuel through the hydrodeoxygenation (HDO) process using aliphatic ether or acid as model compounds [1–5]. HDO of triglycerides, fatty esters and acids produce an oxygen-free mixture of alkanes which are the valuable components compatible with petroleum-based motor fuels [6]. In recent years transition metal phosphide systems have proved to be the promising catalysts in HDO of fatty acid methyl esters [7–16], fatty acids [17] and vegetable oils [5,18] as well as in co-hydroprocessing of vegetable oils and gas oil mixture [19]. Among a number of transition metal phosphides the silica-supported nickel phosphide catalysts were found to display a higher activity in HDO of aliphatic ether [7], which is converted through the complicated scheme with the participation of acid-catalyzed and metal-catalyzed reactions [7,12,14,15,20,21]. Alkanes with the same number of carbon atoms and water are produced in the HDO pathways including hydrogenation-dehydrogenation and dehydration reactions; while DeCO\textsubscript{x} pathways produce alkanes with shorter carbon chains and CO\textsubscript{x} molecules via hydrogenuolysis of C-C bonds.

The catalytic activities of nickel phosphides in hydrogenation and hydrogenuolysis reactions are attributed to their metallic and acidic properties [12,22–25], caused by the covalent nature of Ni-P bond in phosphides and a slight charge transfer from Ni to P [25]. Metal phosphides contain weak
Brønsted and Lewis acid sites attributed to the presence of unreduced \( \text{PO}_x \) groups and the metal sites with small positive charge, respectively [7,26–28]. The various aspects of preparation technique, such as precursor nature, reduction temperature, metal content and Ni/P ratio were observed to affect the physicochemical and catalytic properties of the Ni\(_x\)P\(_y\)/SiO\(_2\) catalyst [24,29–32].

It was stated that the initial Ni/P molar ratio has a profound effect on the structure and catalytic activity of the supported nickel phosphide catalysts obtained with a conventional preparation method by temperature-programmed reduction (TPR) of nickel phosphate precursors [7,8,12,17,18,29,31,33]. Stinner et al. [29] have reported that Ni/P molar ratio equal to 2 leads to the formation of Ni\(_{12}\)P\(_5\) and Ni\(_3\)P phases over silica, Ni/P molar ratio equal to 1.7 leads to Ni\(_{12}\)P\(_5\) and Ni\(_2\)P phases, and Ni/P molar ratio = 1.5 favors Ni\(_3\)P phase only.

Chen et al. [7] studied the silica-supported nickel phosphide catalysts with different Ni/P molar ratios in methyl laurate HDO. It was observed that the catalytic activity of obtained catalysts followed the order:

\[
\text{Ni}_3\text{P } (\text{Ni}/\text{P} = 3/1) < \text{Ni}_{12}\text{P}_5 (\text{Ni}/\text{P} = 2/1) < \text{Ni}_2\text{P} (\text{Ni}/\text{P} = 1/1 \text{ and } 1/2) \approx \text{Ni}.
\]

Yang et al. [8] investigated the influence of Ni/P molar ratios on the performance of Ni\(_x\)P\(_y\)/SBA-15 catalysts in methyl oleate HDO. It was shown that Ni\(_2\)P/SBA-15 catalyst with Ni/P = 1/1 presents the highest catalytic activity; the catalytic activity of nickel phosphide catalysts in methyl oleate HDO followed the order:

\[
\text{Ni}_3\text{P } (\text{Ni}/\text{P} = 3/1) < \text{Ni}_{12}\text{P}_5 (\text{Ni}/\text{P} = 2/1) \approx \text{Ni}_2\text{P} (\text{Ni}/\text{P} = 1/2) < \text{Ni}_2\text{P} (\text{Ni}/\text{P} = 1/1).
\]

It was mentioned that the catalytic activity of Ni/SBA-15 catalyst is slightly higher than demonstrated by any of the similar prepared Ni\(_2\)P/SBA-15 samples in methyl oleate HDO [8,9]. Guan et al. [10] and Xue et al. [11] showed the opposite results on methyl palmitate HDO in the presence of Ni/SiO\(_2\) and Ni\(_2\)P/SiO\(_2\) catalysts. It was pointed [10] that Ni\(_2\)P/SiO\(_2\) showed significantly higher activity in comparison with Ni/SiO\(_2\) in terms of methyl palmitate conversion. The catalytic activity of the Ni\(_x\)P\(_y\)/SiO\(_2\) catalysts depending on Ni/P ratios increases in the order:

\[
\text{Ni}_2\text{P } (\text{Ni}/\text{P} = 1/1.5) < \text{Ni}_2\text{P} (\text{Ni}/\text{P} = 1/1.75) < \text{Ni}_2\text{P} (\text{Ni}/\text{P} = 1/2) < \text{Ni}_2\text{P} \text{ and } \text{Ni}_3\text{P}_4 (\text{Ni}/\text{P} = 1/2.5).
\]

The above-cited articles demonstrate discrepancy in the results concerning the effect of Ni/P ratio on the catalytic properties of nickel phosphide catalysts in methyl ethers HDO. Nearly the same activities in methyl laurate HDO were reported by Chen et al. [7] for the catalysts with the Ni/P ratios 1/1 and 1/2 indicating negligible effect at Ni/P < 1; according to Yang et al. [8] the highest activity in methyl oleate HDO was displayed by the catalyst with Ni/P = 1/1. And, finally, a gradual increase in catalytic activity was observed in the study of Guan et al. [10] with the decrease of Ni/P ratio from 1/1.15 to 1/2.5. This discrepancy can be explained by the use of catalysts with the different metal loading, mean particle sizes or wide particle size distribution, which could have influenced the catalytic activity. The scarce data on size effect are also rather contradictory. According to data reported by Guan et al. [13] the particle size increase of MCM-41 supported nickel phosphide has no influence on TOF of methyl palmitate conversion. Yang et al. [14] reported that the TOF increased with the Ni\(_3\)P crystallite size in the methyl laurate HDO.

To reach a better insight into the Ni/P effect on the catalytic properties of silica-supported nickel phosphide catalysts in methyl palmitate HDO two sets of Ni\(_x\)P\(_y\)/SiO\(_2\) catalysts differing in Ni content and Ni/P ratio were used in the present study [15]. The low-loaded catalysts (about 2.5 wt % of nickel) with nearly the same mean particle size are the appropriate candidates for the comparison of specific activities of the Ni\(_x\)P\(_y\)/SiO\(_2\) catalysts with the Ni/P ratios 2:1, 1:1 and 1:2. The high-loaded samples (about 9–10 wt % of nickel) were used to follow the evolution of the active phase with the
Ni/P decrease the X-Ray Diffraction (XRD), transmission electron microscopy (TEM) and P\textsuperscript{31} nuclear magnetic resonance (NMR) techniques were employed.

2. Results and Discussion

2.1. Catalysts Characterization

Two sets of the Ni\textsubscript{x}P\textsubscript{y}/SiO\textsubscript{2} catalysts were prepared with different initial Ni/P molar ratios and nickel content in each series in the range of 2.5–2.9 wt % (denoted as low-loaded samples, l-Ni\textsubscript{x}P\textsubscript{y}) or 9.0–10.9 wt % (denoted as high-loaded samples, h-Ni\textsubscript{x}P\textsubscript{y}). For the preparation of each set of the catalysts the solutions of nickel acetate (Ni(CH\textsubscript{3}COO)\textsubscript{2}) and di-ammonium hydrogen phosphate ((NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4}) were used, containing the adjusted amount of Ni and different initial Ni/P molar ratios of 2/1; 1/1 or 1/2. The obtained samples were denoted as h-Ni2P1, h-Ni1P1, h-Ni1P2 and l-Ni2P1, l-Ni1P1, l-Ni1P2, correspondingly.

Recently Shamanaev et al. [16] established the optimal reduction conditions for the silica-supported nickel phosphide catalysts displaying the highest catalytic activity in methyl palmitate hydrodeoxygenation. On the basis of our previous results [15,16] and the literature data reported for the phosphate-containing type of precursors [13,34–36] the reduction temperature of 600 °C was chosen in this study for catalysts preparation. The physicochemical properties of the Ni\textsubscript{x}P\textsubscript{y}/SiO\textsubscript{2} catalysts as well as PO\textsubscript{x}/SiO\textsubscript{2} reference sample, and SiO\textsubscript{2} support are summarized in Table 1.

Table 1. Physicochemical properties of Ni\textsubscript{x}P\textsubscript{y}/SiO\textsubscript{2} catalysts as well as the reference samples Ni/SiO\textsubscript{2}, PO\textsubscript{x}/SiO\textsubscript{2} and SiO\textsubscript{2} support.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni, wt %</th>
<th>P, wt %</th>
<th>Ni/P Molar Ratio after TPR</th>
<th>A\textsubscript{BET}, m\textsuperscript{2}/g</th>
<th>D\textsubscript{pore}, nm</th>
<th>D\textsubscript{S after TPR}, nm</th>
<th>X-ray Diffraction (XRD) Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>300</td>
<td>10.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PO\textsubscript{x}/SiO\textsubscript{2}</td>
<td>-</td>
<td>5.31</td>
<td>-</td>
<td>200</td>
<td>10.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>h-Ni</td>
<td>8.6</td>
<td>-</td>
<td>-</td>
<td>215</td>
<td>10.5</td>
<td>Ni</td>
<td>Ni\textsubscript{12}P\textsubscript{5}</td>
</tr>
<tr>
<td>h-Ni2P1</td>
<td>10.9</td>
<td>2.4</td>
<td>2.4</td>
<td>195</td>
<td>11.7</td>
<td>Ni\textsubscript{12}P\textsubscript{5}</td>
<td>Ni\textsubscript{2}P</td>
</tr>
<tr>
<td>h-Ni1P1</td>
<td>10.3</td>
<td>3.6</td>
<td>1.5</td>
<td>190</td>
<td>10.4</td>
<td>Ni\textsubscript{2}P</td>
<td>Ni\textsubscript{2}P</td>
</tr>
<tr>
<td>h-Ni1P2</td>
<td>9.0</td>
<td>5.0</td>
<td>0.9</td>
<td>175</td>
<td>10.3</td>
<td>Ni\textsubscript{2}P</td>
<td>Ni\textsubscript{2}P</td>
</tr>
<tr>
<td>l-Ni2P1</td>
<td>2.9</td>
<td>0.8</td>
<td>2.1</td>
<td>290</td>
<td>10.1</td>
<td>4.9 ± 1.3</td>
<td>Ni\textsubscript{12}P\textsubscript{5}</td>
</tr>
<tr>
<td>l-Ni1P1</td>
<td>2.8</td>
<td>1.4</td>
<td>1.1</td>
<td>270</td>
<td>10.3</td>
<td>4.7 ± 1.1</td>
<td>Ni\textsubscript{2}P</td>
</tr>
<tr>
<td>l-Ni1P2</td>
<td>2.5</td>
<td>1.9</td>
<td>0.7</td>
<td>255</td>
<td>10.5</td>
<td>3.5 ± 0.9</td>
<td>Ni\textsubscript{2}P</td>
</tr>
</tbody>
</table>

According to the elemental analysis by ICP-AES, the Ni content in reduced samples varied from 2.5 to 2.9 wt % for the low-loaded set of samples (l-Ni\textsubscript{x}P\textsubscript{y}) and from 8 to 11 wt % for the high-loaded set of samples (h-Ni\textsubscript{x}P\textsubscript{y}). It was stated that the Ni/P molar ratios in reduced catalysts were higher than the initial Ni/P molar ratios in oxide precursors and impregnating solutions. The increase of the Ni/P molar ratio in the samples after reduction is caused by the formation of volatile phosphorus-containing species (namely PH\textsubscript{3}, P, P\textsubscript{2} etc.) during high-temperature reduction as it has been reported earlier [31].

The textural parameters of the reduced catalysts have been obtained from the N\textsubscript{2} adsorption-desorption isotherms (Table 1). The BET specific surface areas (A\textsubscript{BET}) of the low-loaded set of samples decrease slightly with nickel phosphide loading in comparison with the pure SiO\textsubscript{2} support (255–290 m\textsuperscript{2}/g vs. 300 m\textsuperscript{2}/g of SiO\textsubscript{2}); the decrease of the BET surface areas for the high-loaded set of samples is more pronounced (175–195 m\textsuperscript{2}/g), indicating the partial coverage and/or clogging of the inner pore space of the catalysts by the nickel phosphide particles and residues of the phosphorus-containing compounds (unreduced PO\textsubscript{x} groups [30,37], elemental P\textsubscript{4} and P\textsubscript{2} [29]). It was observed that with decreasing of the Ni/P ratio in each set of the reduced catalysts, the surface area and pore volume tended to decrease because of the surplus phosphorus-containing species on
silica surface [29,38]. The average pore diameters for the \( l-Ni_{x}P_{y} \) and \( h-Ni_{x}P_{y} \) sets of catalysts do not changed noticeably (Table 1).

The formation of nickel phosphide particles on silica surface after temperature-programmed reduction (TPR) was proved by XRD, TEM and \(^{31}\)P-MAS NMR methods. The X-ray diffraction patterns of reduced \( Ni_{x}P_{y}/SiO_{2} \) catalysts and \( SiO_{2} \) support are presented in Figure 1. XRD pattern of the initial \( SiO_{2} \) support (Figure 1a) contains a broad peak centered at \( 2\theta \approx 22^\circ \), which corresponds to amorphous \( SiO_{2} \) and can be seen in all of the represented XRD patterns of the \( Ni_{x}P_{y}/SiO_{2} \) catalysts. Figure 1a shows the XRD patterns of the high-loaded \( h-Ni2P1 \) and low-loaded \( l-Ni2P1 \) samples that were prepared with the initial \( Ni/P \) molar ratio equal to 2/1. Apart from the diffraction peak related to the support, the characteristic peaks at \( 2\theta = 32.6^\circ, 38.4^\circ, 41.7^\circ, 44.4^\circ, 46.9^\circ \) and \( 48.9^\circ \) of the \( Ni_{12}P_{5} \) phase (\( a = b = 8.646 \ \AA, \ c = 5.070 \ \AA, \ \alpha = \beta = \gamma = 90^\circ; \ \)JCPDS #22-1190) are fixed in the diffraction patterns of \( Ni2P1 \) samples. The estimation of \( Ni_{12}P_{5} \) crystallites size (\( D_{\text{XRD}} \)) on the surface of the high-loaded \( h-Ni2P1 \) sample gives about 16.0 nm, whereas the XRD pattern of low-loaded \( l-Ni2P1 \) sample contains very weak and broadened reflections from \( Ni_{12}P_{5} \) phase, suggesting that this phase should be highly dispersed (Figure 1a). That makes difficult the correct determination of \( D_{\text{XRD}} \) for \( l-Ni2P1 \) sample.

Figure 1b shows the XRD patterns of the high-loaded \( h-Ni1P1 \) and low-loaded \( l-Ni1P1 \) samples prepared with equimolar initial \( Ni/P \) ratio. All of represented XRD patterns of \( Ni1P1 \) catalysts contain the characteristic peaks at \( 2\theta = 40.6^\circ, 44.5^\circ, 47.1^\circ, 54.1^\circ, 54.8^\circ, 66.1^\circ, 72.5^\circ \) and \( 74.5^\circ \) of the \( Ni_3P \) phase (\( a = b = 5.859 \ \AA, \ c = 3.382 \ \AA, \ \alpha = \beta = \gamma = 90^\circ; \ \)JCPDS #03-0953) with \( D_{\text{XRD}} = 13 \) nm for \( h-Ni1P1 \) sample. The XRD patterns of the high-loaded \( h-Ni1P2 \) and low-loaded \( l-Ni1P2 \) samples prepared with the lower initial molar \( Ni/P = 1/2 \) are displayed in Figure 1c. The \( Ni_3P \) phase characteristic peaks are revealed in the diffraction patterns of \( Ni1P2 \) samples with the estimated \( Ni_3P \) crystallites size equal to \( D_{\text{XRD}} = 10 \) nm in the \( h-Ni1P2 \) sample. The diffraction patterns corresponding to \( l-Ni1P2 \) samples exhibits the broadened diffraction lines with a lower intensity indicating the presence of the highly dispersed \( Ni_3P \) phase. Also, as for the other low-loaded samples, it is hardly possible to estimate \( D_{\text{XRD}} \) for \( l-Ni1P2 \) sample from the XRD data correctly.

![Figure 1](image-url)

**Figure 1.** XRD patterns of silica-supported \( Ni_{x}P_{y} \) catalysts and \( SiO_{2} \) support: (a) \( h-Ni2P1, l-Ni2P1 \) and \( SiO_{2} \); (b) \( h-Ni1P1 \) and \( l-Ni2P1 \); (c) \( h-Ni1P2, l-Ni1P2 \).
Thus, the XRD data are shown in Table 1 and Figure 1 clearly demonstrate that the initial Ni/P molar ratio influences crystalline phase composition of the reduced phosphide catalysts. The initial Ni/P molar ratio of 2/1 favors formation of Ni$_{12}$P$_5$ phase. Further increasing the amount of phosphorus to Ni/P = 1/1 and 1/2 led to the formation of the Ni$_2$P phase. A similar dependence of nickel phosphide crystalline phase on the initial Ni/P molar ratio for silica-supported nickel phosphide catalysts has been observed previously for phosphate precursor [7,8,37,38]. The initial excess of P content in the precursors was shown to be the prerequisite of the Ni$_2$P phase formation [7,8,30,31,37,38].

The increase of phosphorus precursor content in the Ni$_3$P/SiO$_2$ catalysts leads to a higher dispersion of nickel phosphide particles on a silica support. The nickel phosphide crystallite sizes for the high-loaded set of the samples diminishes in the row: $h$-Ni$_2$P1 (16.0 nm) > $h$-Ni1P1 (13.0 nm) > $h$-Ni1P2 (10.0 nm). Probably the initial nickel phosphate precursor was surrounded with an excess of polymeric phosphate species preventing the aggregation during the calcination step and favoring the higher dispersion of resulting nickel phosphide particles [31].

The TEM images of two sets of the Ni$_x$P$_y$/SiO$_2$ catalysts with different initial Ni/P molar ratios are shown in Figure 2a–f. The nickel phosphide particles with different size ranged in the regions from 2.0 to 20 nm were observed in the high-loaded $h$-Ni2P1, $h$-Ni1P1 and $h$-Ni1P2 samples (Figure 2a–c). Besides, several particles with the size up to 50 nm were found. The observed wide particle size distribution makes it difficult to estimate correctly the average size of particles by statistical analysis of the TEM patterns of $h$-Ni$_x$P$_y$ samples. The TEM images of the low-loaded $l$-Ni2P1, $l$-Ni1P1, and $l$-Ni1P2 catalysts (Figure 2d–f) show the nickel phosphide particles with a narrow particle size distribution; the mean particle surface diameters ($D_s$) are 4.9 ± 1.3 nm for $l$-Ni2P1, 4.7 ± 1.1 nm for $l$-Ni1P1 and 3.5 ± 0.9 nm for $l$-Ni1P2. The TEM image of $l$-Ni2P1 sample (see Figure S1a in Supplementary Materials) reveals crystal lattice fringes with the d-spacing value of 2.20 Å, 2.47 Å, and 2.74 Å corresponding to the (202), (112) and (220) reflections of the Ni$_{12}$P$_5$ phase (JCPDS #22-1190), respectively. The TEM images of $l$-Ni1P1 and $l$-Ni1P2 samples in Figures S1b and S1c in Supplementary Materials exhibit crystal lattice fringes with the d-spacing value of 2.24 Å, 2.05 Å, and 1.92 Å corresponding to the (111), (201), and (120) reflections of the Ni$_2$P crystalline phase (JCPDS #03-0953).

To explore the nature of the phosphorus species on the reduced nickel phosphide catalysts the $^{31}$P MAS NMR technique was employed. Prior to NMR experiments, nickel phosphide catalysts after reduction by the conventional TPR procedure at 600 °C were transferred into ampoules and further to NMR rotor in a glove box under argon atmosphere to avoid the contact with air. This technique helps to avoid possible oxidation of nickel phosphide during NMR spectra acquisition. Figure 3 demonstrates a spin-echo $^{31}$P 14 kHz MAS NMR spectra of the high-loaded $h$-Ni2P1, $h$-Ni1P1 and $h$-Ni1P2 catalysts with different initial Ni/P molar ratio. Two main regions of the spectra of all the measured nickel phosphide catalysts can be highlighted. The first region from +500 to +5000 ppm corresponds to Ni-P intermetallic compounds such as Ni$_{12}$P$_5$, Ni$_3$P, Ni$_2$P, NiP, and Ni$_3$P$_4$ [15,29,39] and the second one from +4 to −40 ppm corresponds to the different phosphate species (denoted in this study overall as PO$_x$ groups), i.e., phosphoric acid H$_n$PO$_{4(3−n)}$− (−0 ppm), terminal P$_2$O$_7^{4−}$ (−−7 ppm), and internal (PO$_3^{−}$)$_n$ (−−22 ppm) phosphate groups in phosphoric acid oligomers [15,29,32,40,41]. For all of the applied catalysts, we detected the lack of the signals with chemical shifts from −30 to −50 ppm that could be attributed to phosphorus-containing species in the form of silicon phosphate [40].
The $^{31}$P NMR spectrum of $h$-Ni2P1 sample in Figure 3 shows two well-resolvable signals with isotropic chemical shifts at $\sim$1950 and $\sim$2250 ppm corresponding to Ni$_{12}$P$_5$ phase [29]. This observation agrees with the crystalline structure identified by XRD (Table 1). Also, the additional signals from other Ni-P intermetallic compounds at 900–1500 ppm chemical shifts region are revealed in the spectrum of $h$-Ni2P1 sample. However, the amount of this new phase is negligible (since the exact line shape of Ni$_{12}$P$_5$ is not known the precise ratio cannot be extracted). The amount of the phosphorus species in the form of PO$_x$ groups ($\omega$(PO$_x$)) was determined from the intensities of signals in the chemical shifts region from +4 to $-40$ ppm. It was found that $\omega$(PO$_x$) = 3.5 at % for $h$-Ni2P1 sample.

The Ni$_2$P structure contains two crystallographic P sites and consequently gives two resonances with isotropic chemical shifts of 1487 and 4076 ppm [29]. The $^{31}$P NMR spectra of $h$-Ni1P1 and $h$-Ni1P2 samples in Figure 3 show two signals with isotropic chemical shifts at $-1500$ and $-4050$ ppm, confirming the Ni$_2$P phase formation. The observed broad signal with a maximum at $-1500$ ppm is not symmetric, most probably due to the superposition of several signals, the NMR line shape effects could also be a reason. The maximum at $-1500$ ppm is most likely to corresponds to Ni$_2$P phase; nevertheless, the presence of other Ni-P intermetallic compounds as Ni$_{12}$P$_5$, Ni$_3$P, NiP, and Ni$_5$P$_4$ [29,39] cannot be
avoided since their chemical shifts lie in the same region and the large full width at a half maximum (FWHM) does not provide good separation of the lines. The large FWHM can be a result of either small particle or inhomogeneous character (defectiveness) of Ni-P intermetallic compounds.

The \textit{h}-Ni1P1 sample shows two different phosphorus sites of Ni$_2$P in contrast to \textit{h}-Ni1P2 sample for which both the lines are highly broadened. The downfield line shoulder is not observed in \textit{h}-Ni1P1 sample either. Moreover, the line FWHM is narrower, which causes observation of spinning sidebands. It was found that the characteristic lines at \textasciitilde 1500 and \textasciitilde 4050 ppm in \textsuperscript{31}P NMR spectrum of \textit{h}-Ni1P1 sample are narrower than those for \textit{h}-Ni1P2 sample probably because of smaller amount of stacking faults in \textit{h}-Ni1P1 sample or larger average nickel phosphide particle size that leads to presence of some amount of large particles with well-formed Ni$_2$P phase giving rise to sharp peaks on the spectrum. The estimated values of $\omega$(PO$x$) are equal to 10.0 and 13.0 at % of total phosphorus for \textit{h}-Ni1P1 and for \textit{h}-Ni1P2 samples correspondingly. It is necessary to mention that \textsuperscript{31}P NMR spectrum of low-loaded \textit{l}-NiP2 sample resembles the spectrum of \textit{h}-Ni1P2 catalyst, but intensities of the peaks in the low-loaded sample are noticeably lower, which makes questionable the quantitative estimation of the amount of PO$_x$ groups.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.pdf}
\caption{Spin-echo \textsuperscript{31}P 14 kHz MAS NMR spectra of high-loaded Ni$_x$P$_y$/SiO$_2$ catalysts with different initial Ni/P molar ratio (2/1, 1/1 and 1/2 top-down) reduced at 600 °C. Spectra are normalized to the same amplitude of the highest point.}
\end{figure}

Summarizing the XRD, TEM and NMR results of catalysts characterization the several conclusions have to be indicated. XRD and \textsuperscript{31}P MAS NMR data showed that the initial Ni/P molar ratio influences on phase composition of reduced phosphide catalysts: Ni$_2$P is produced using the initial Ni/P molar ratio of 1 and 0.5, while the initial Ni/P molar ratio of 2 favors formation of Ni$_{12}$P$_5$ phase in accordance with the previous results \cite{7,8,37,38}. The TEM data showed that high-loaded samples (\textit{h}-Ni2P1, \textit{h}-Ni1P1, and \textit{h}-Ni1P2) contain phosphide particles with the broad particle size distribution (from 2 to 20 nm). On the contrary, the TEM images of the low-loaded samples demonstrated uniformly distributed phosphide particles with approximately the same mean particle diameter. \textsuperscript{31}P MAS NMR results let us estimate the portion of P entering in the PO$_x$ groups on the surface of high-loaded samples, showing the enrichment of the catalysts with phosphate species as the Ni/P ratio decreases.
Unfortunately, such estimation cannot be done in the case of the low-loaded samples due to the low intensity of the $^{31}$P MAS NMR signals. Previously it was stated that namely the PO$_x$ groups are responsible for the Brønsted acidity of Ni$_x$P$_y$/SiO$_2$ catalysts [7,26,28,37,42,43].

The obtained set of low-loaded samples are the appropriate candidates for comparing catalytic behavior in methyl palmitate hydrodeoxygenation due to approximately the same mean particle diameters and narrow particle size distributions of the nickel phosphate on silica. At the same time, high-loaded samples provide a reliable insight into the nature of the active phase in nickel phosphate catalysts.

2.2. Catalytic Performance of Nickel and Nickel Phosphide Catalysts

2.2.1. Mass-Transfer Process in Methyl Palmitate HDO

In order to evaluate the effect of internal diffusion on catalytic HDO, the Weisz-Prater criterion was used [44]. For negligible diffusional limitations the Weisz-Prater number estimated by equations is less than 0.3:

$$ N_{W-P} = \frac{A_{M.S.} \cdot R_{\text{particles}}^2}{C_S \cdot D_{\text{eff}}} \leq 0.3 \quad (1) $$

where $A_{M.S.}$ is the observed reaction rate, $R_{\text{particles}}$ is the catalyst particles radius, $C_S$ is the reactant surface concentration and $D_{\text{eff}}$ is the effective diffusion coefficient. The details of the procedure used for calculation of the Weisz-Prater numbers in case of methyl palmitate HDO was described previously in reference [15]. The Weisz-Prater numbers for hydrogen and methyl palmitate for the most active high-loaded $h$-Ni1P2 sample in methyl palmitate HDO were found at a temperature of 290 °C, hydrogen pressure 3.0 MPa, H$_2$/feed volume ratio 600 Nm$^3$/m$^3$ and LHSV of 10.7 h$^{-1}$. The values of $N_{W-P, H_2} = 0.02$ and $N_{W-P, MP} = 0.16$ indicate the negligible internal mass transfer effects on HDO rate.

2.2.2. Catalytic Performance of Nickel Phosphide Catalysts in Methyl Palmitate HDO

Catalytic properties of nickel phosphide catalysts were investigated in the HDO of methyl palmitate (10 wt % methyl palmitate in n-dodecane) in a trickle-bed reactor at a temperature of 290 °C, hydrogen pressure 3.0 MPa, H$_2$/feed volume ratio 600 Nm$^3$/m$^3$, LHSV of methyl palmitate varied in the interval from 0.3 to 16 h$^{-1}$. The X$_{MP}$—LHSV dependencies were obtained to follow the evolution of methyl palmitate (MP), intermediates and the end products in the course of the reaction. The reaction rates normalized per gram of catalysts ($A_{\text{HDO}}$) and per metal sites (TOF) were calculated at the MP conversion level about 15–20% (for details see Section 3.3).

The catalytic properties of silica-supported Ni phosphide catalysts with different initial Ni/P molar ratio and Ni content are summarized in Table 2. The comparison of the rate of MP transformation ($A_{\text{HDO}}$) over two sets of catalysts let us see that $A_{\text{HDO}}$ is lower over the high-loaded sample with the same Ni/P ratio. Decreasing of Ni/P molar ratio favors increasing of $A_{\text{HDO}}$ over both high- and low-loaded samples (Figure 4). Broad particle size distributions of phosphate phases on the surfaces of high-loaded $h$-Ni2P1, $h$-Ni1P1, and $h$-Ni1P1 samples does not allow us to compare the activity of these catalysts calculated per metal site (TOF). The TOF were calculated for the samples with nearly the same size of Ni phosphide nanoparticles ($l$-Ni2P1, $l$-Ni1P1, and $l$-Ni1P2). The trend is the same as for $A_{\text{HDO}}$—with the decrease of Ni/P molar ratio TOF increases visibly from 5.31 s$^{-1}$ over $l$-Ni2P1 to 10.65 s$^{-1}$ over $l$-Ni1P1 and 14.3 s$^{-1}$ over $l$-Ni1P2. The difference in the activities of $l$-Ni2P1 and the other samples can be explained by the difference in the active phase composition (Ni$_{12}$P$_3$ versus Ni$_2$P), but both $l$-Ni1P1 and $l$-Ni1P2 samples contain Ni$_3$P phase. The main difference between these two samples is the lower Ni/P ratio in the $l$-Ni1P2 samples, while the mean sizes of Ni phosphate particles are similar. In turn, the decrease of Ni/P ratio led to the of phosphate groups content on the surface of phosphate catalysts (Figure 3).
### Table 2. Catalytic properties of silica-supported nickel and nickel phosphide catalysts in methyl palmitate HDO. Reaction conditions: $P_{\text{H}_2} = 3.0$ MPa, $T = 290$ °C, $H_2/$feed = 600 Nm$^3$/Nm$^3$, LHSV = 1.5–16.0 h$^{-1}$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni/P Molar Ratio in Precursor</th>
<th>XRD Phase</th>
<th>$A_{\text{HDO}}$ (mol/(h·g$_{\text{Ni}}$))</th>
<th>$A_{\text{MS}}$·10$^3$ s$^{-1}$</th>
<th>$S_{\text{160}}$, %</th>
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</thead>
<tbody>
<tr>
<td>$h$-Ni</td>
<td>-</td>
<td>Ni</td>
<td>8.8 × 10$^{-3}$</td>
<td>12.7</td>
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</tr>
<tr>
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<td>3.4 × 10$^{-2}$</td>
<td>28.0</td>
<td></td>
</tr>
<tr>
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<td>Ni$_2$P</td>
<td>8.2 × 10$^{-2}$</td>
<td>28.8</td>
<td></td>
</tr>
<tr>
<td>$h$-Ni1P2</td>
<td>0.5</td>
<td>Ni$_2$P</td>
<td>1.8 × 10$^{-1}$</td>
<td>32.8</td>
<td></td>
</tr>
<tr>
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<td>2</td>
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<td>7.6 × 10$^{-2}$</td>
<td>5.31</td>
<td>25.8</td>
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<tr>
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<td>Ni$_2$P</td>
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<td>10.65</td>
<td>32.1</td>
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<tr>
<td>$l$-Ni1P2</td>
<td>0.5</td>
<td>Ni$_2$P</td>
<td>2.5 × 10$^{-1}$</td>
<td>14.33</td>
<td>31.5</td>
</tr>
</tbody>
</table>

**Figure 4.** $A_{\text{HDO}}$ (mol/(h·g$_{\text{Ni}}$)) versus PO$_x$ (at %) for the catalysts with different Ni/P molar ratios: Ni2P1, Ni1P1, and Ni1P2. Catalytic activity. $A_{\text{HDO}}$, of 2.5 wt % Ni$_x$P$_y$/SiO$_2$ and 7.0 wt % Ni$_x$P$_y$/SiO$_2$ catalysts prepared with different Ni:P molar ratios in methyl palmitate HDO at the temperature = 290 °C and hydrogen pressure = 3.0 MPa. For the series of 7.0 wt % Ni$_x$P$_y$/SiO$_2$ catalysts ($h$-Ni2P1, $h$-Ni1P1, and $h$-Ni1P2) it was pointed the amount of PO$_x$ (at %) determined by $^{31}$P magic angle-spinning (MAS) nuclear magnetic resonance (NMR).

So, the obtained results have shown the increase of catalytic activity of silica-supported phosphide catalysts in methyl palmitate HDO with the decrease of Ni/P ratio in the sets of catalysts with nearly the same Ni content. This trend coincides with the increase of the PO$_x$ groups’ content percentage observed by NMR in high-loaded samples with the decrease of Ni/P ratio (3.5, 10 and 13 at % of the total P content in the $h$-Ni2P1, $h$-Ni1P1, and $h$-Ni1P2). Unfortunately, the quantitative estimation of the amount of PO$_x$ groups in the low-loaded sample is questionable because of the low intensities of the corresponding signals. But considering the similarity in the phase composition and TPR profile (see Figure S2 in Supplementary Materials) between the low- and high-loaded samples with the close Ni/P ratio, we can presume the same trend of PO$_x$ groups’ dependence on Ni/P ratio in both sets of catalysts. The evolution of catalytic activity with the Ni/P ratio can be explained by the change of the amount of PO$_x$ surface groups, taking into account the tentative scheme of methyl palmitate conversion and the possible role of PO$_x$ groups that is known to display Brønsted acidity in the Ni$_x$P$_y$/SiO$_2$ catalysts [7,26,28,37,42,43].

The tentative reaction network of MP transformation over silica-supported Ni phosphide catalysts is considered, taking into account the liquid product distribution, the gas phase analysis and the literature data concerning the HDO of fatty acid ethers [7,10,12–14]. The reaction network of methyl palmitate HDO (Figure 5) has been proposed including several types of reactions which can occur over metal (hydrogenation-dehydrogenation, hydrogenolysis of C-O and C-C bonds) and acid (hydrolysis, esterification, dehydration) active sites [14]. The analysis of product distribution
depending on LHSV shows that the main products of methyl palmitate HDO are C\textsubscript{15} and C\textsubscript{16} alkanes, while only minor quantities of intermediate O-containing products, namely palmitic acid, hexadecanal, hexadecanol and palmityl palmitate are detected in all the experiments regardless of the Ni content and Ni/P ratio (Figures 6–8). The formation of negligible amounts of O-containing intermediates is confirmed by a minor difference between the conversion of methyl palmitate and overall conversion of oxygen-containing compounds defined by CHNSO elemental analysis (Figure 9). These observations indicate that the oxygen-containing intermediates are transformed further immediately after their production from methyl palmitate, that is, the transformation of methyl palmitate limits of the overall HDO reaction producing C\textsubscript{15} and C\textsubscript{16} alkanes as the end products. As a consequence, first of all, the possible routes of methyl palmitate conversion to the intermediates should be analyzed.

Figure 5. Proposed reaction network over silica-supported nickel phosphide catalysts.

It was proposed in many studies \[2,4,7,10,13,14,45\] that methyl palmitate transformation proceeds through the formation of palmitic acid or hexadecanal as a primary intermediate (Figure 5). Both possibilities exist for the production of palmitic acid in the HDO of methyl palmitate: via the hydrogenolysis of the C-O bond of ester group over metal sites with the formation of CH\textsubscript{4} along with acid or through acid-catalyzed hydrolysis of ester with water leading to the formation of methanol. Hexadecanal can be formed through the direct hydrogenolysis of the C-O σ-bond of the methyl palmitate carboxylic group leading to hexadecanal and methanol: the second possible way of hexadecanal formation involves hydrogenation of palmitic acid, accompanied with the production of water. Among the listed transformation of methyl palmitate only hydrolysis requires the acid functionality, so the increase of the PO\textsubscript{x} groups amount in the row of catalysts Ni\textsubscript{2}P\textsubscript{1} < Ni\textsubscript{1}P\textsubscript{1} < NiP\textsubscript{2} the acceleration of methyl palmitate transformation due to the acid-catalyzed hydrolysis. Several research groups have already reported an increase of Bronsted acid site quantities determined by means of NH\textsubscript{3}-TPD techniques and assigned to P-OH species with the decrease of Ni/P ratio in the silica-supported nickel phosphide catalysts \[7,28,37,42,43\].

In our experiments, the \textit{h-NixP\textsubscript{y}} catalysts displayed a higher activity in methyl palmitate HDO that supported Ni/SiO\textsubscript{2} catalyst (D\textsubscript{BET} = 10.7 nm) with nearly the same content of nickel (Figure 10). While Ni/SiO\textsubscript{2} catalyst produces pentadecane with the selectivity about 90% in all range of the experiments, SiO\textsubscript{2} and PO\textsubscript{x}/SiO\textsubscript{2} produce only palmitic acid as a result of acid-catalyzed hydrolysis of MP. Additional amount of dodecanol causes the decrease of the rate of MP transformation when HDO of MP and dodecanol mixture was performed over the \textit{t-Ni1P2} catalyst (see Figure S3 in Supplementary Materials), pointing out to the competition of dodecanol with the MP molecules.
for the acid sites and testifying the participation of these sites in the MP conversion. The above observations confirm implicitly the important role of acid sites in the methyl palmitate transformation to the intermediates. The analysis of products distribution in the gas phase provides additional information about possible reaction routes of MP and oxygen-containing intermediates transformation. Among the gas phase products of methyl palmitate HDO methane, CO and some amounts of methanol were observed. The absence of CO2 in the outlet gas indicates that palmitic acid does not produce the C15 hydrocarbons through the decarboxylation (DeCO2) route. Further conversion of acid most probably proceeds through the hydrogenation to hexadecanal which in turn gives n-pentadecane and n-pentadecene through decarbonylation reaction or hexadecanol through hydrogenation reaction. The latter is the main source of C16 paraffin via elimination of water from hexadecanol with the formation of hexadecene and subsequent hydrogenation of hexadecene to n-hexadecane [15]. Obtained data on selectivity in methyl palmitate HDO correlate well with gas phase data: CO concentration in the gas phase is proportional to n-pentadecane content in the liquid products (see Figure S4 in Supplementary Materials). Authors [7,12,14] reported decarbonylation of methyl laurate (with the formation of undecene) or lauric acid (producing undecanol) but we do not have any evidence that these reactions take place. Moreover, the decarbonylation of palmitic acid should produce alcohol with 15 carbon atoms, but oxygen-containing compounds with 15 carbon atoms in hydrocarbon chain were not detected. Instead, pentadecene was found among the reaction products in small amounts, pointing out to the possibility of hexadecanol decarbonylation producing pentadecene and pentadecane (Figure 5). So, the observed peculiarities make hexadecanal the most probable source of C15 hydrocarbons.

![Figure 6](image1.png)

**Figure 6.** Concentration profiles of liquid-phase components during methyl palmitate HDO over l-Ni2P1 catalyst: (a) the main products—C15 and C16 hydrocarbons; (b) the observed intermediates. Reaction conditions: \( P_{\text{H2}} = 3.0 \text{ MPa}, T = 290 \degree C, H_2/\text{feed} = 600 \text{Nm}^3/\text{Nm}^3, \text{LHSV} = 0.3–1.5 \text{ h}^{-1} \).

![Figure 7](image2.png)

**Figure 7.** Concentration profiles of the liquid-phase components during methyl palmitate HDO over l-Ni1P1 catalyst: (a) the main products—C15 and C16 hydrocarbons; (b) the observed intermediates. Reaction conditions: \( P_{\text{H2}} = 3.0 \text{ MPa}, T = 290 \degree C, H_2/\text{feed} = 600 \text{Nm}^3/\text{Nm}^3, \text{LHSV} = 0.3–3.2 \text{ h}^{-1} \).
the minor effect of the phosphate groups on the C\textsubscript{15} causing the agglomeration of methanol with the produced water.

observed among the product of methyl palmitate HDO can be produced through the methyl palmitate

\[ \text{LHSV} = 0.3–6.4 \text{ h}^{-1} \]

Figure 8. Concentration profiles of the liquid-phase components during methyl palmitate HDO over l-Ni1P2 catalyst: (a) the main products—C\textsubscript{15} and C\textsubscript{16} hydrocarbons; (b) the observed intermediates. Reaction conditions: P\textsubscript{H2} = 3.0 MPa, T = 290 °C, H\textsubscript{2}/feed = 600 Nm\textsuperscript{3}/Nm\textsuperscript{3}, LHSV = 0.3–6.4 h\textsuperscript{-1}.

Figure 9. Methyl palmitate (X\textsubscript{MP}) and oxygen (X\textsubscript{OCC}) conversions versus liquid hourly space velocity (LHSV) of MP (h\textsuperscript{-1}) over the low-loaded nickel phosphate catalysts with different Ni/P molar ratios: l-Ni2P1, l-Ni1P1 and l-Ni1P2. Reaction conditions: P\textsubscript{H2} = 3.0 MPa, T = 290 °C, H\textsubscript{2}/feed = 600 Nm\textsuperscript{3}/Nm\textsuperscript{3}, LHSV = 0.3–6.4 h\textsuperscript{-1}.

To clarify the routes of acid transformation the additional experiments were done using lauric acid as a model compound. Just only CO was observed in the exhaust gas of lauric acid HDO over the l-Ni1P2 catalyst, wherein CO does not give methane at least up to 360 °C (Figure 11). So, methane observed among the product of methyl palmitate HDO can be produced through the methyl palmitate hydrogenolysis or as a result of methanol hydrogenation. The choice between these two contributions is rather complicated since the quantitative analysis of methanol is failed due to its hydrophilicility causing the agglomeration of methanol with the produced water.

Selectivity of methyl palmitate conversion to C\textsubscript{15} and C\textsubscript{16} hydrocarbon (at overall oxygen conversion of 100%) does not display the evident dependence on the Ni/P ratio (Table 2), indicating the minor effect of the phosphate groups on the C\textsubscript{16}/C\textsubscript{15} selectivity. The most active l-Ni1P2 catalyst demonstrated stable behavior in the time-on-stream experiments at least for 15 h (see Figure S5 in Supplementary Materials).
3. Materials and Methods

3.1. Catalyst Preparation

Commercial spherical silica «KSKG» (Salavat, Russia, pore volume—0.80 cm³/g, average pore diameter—10.6 nm) was purchased from «ChromAnalit» Ltd. (Moscow, Russia) and has been used as a support. Prior to use, the silica was dried at 110 °C for 7 h and calcined at 500 °C for 4 h. Afterwards, it was crushed and sieved to 0.25–0.50 mm.

NiₓPᵧ/SiO₂ catalysts synthesis. The silica-supported nickel phosphide catalysts were prepared by temperature-programmed reduction (TPR) of nickel- and phosphate-containing precursors, with varying initial Ni/P molar ratio, namely 2/1, 1/1 and 1/2 (samples were denoted as Ni2P1, Ni1P1, and Ni1P2, correspondingly). The optimal reduction conditions for the NiₓPᵧ/SiO₂ catalysts prepared from the nickel phosphate precursors were chosen according to the earlier results [15] and were stated to 600 °C for 1 h. The initial amount of nickel precursor in the impregnated solution for synthesized...
catalyst was $2.1 \times 10^{-3}$ mol of Ni per gram of support for high-loaded samples (denoted as $h$ series) or $5.2 \times 10^{-4}$ mol of Ni per gram of support for low-loaded samples (denoted as $l$ series). The procedure for catalyst preparation follows: silica (0.25–0.50 mm) was incipiently impregnated with an aqueous solution of Ni(CH$_3$COO)$_2$$\cdot$4H$_2$O («Reakhim», Samara, Russia, 99.5%) and (NH$_4$)$_2$HPO$_4$ («Alfa Aesar», Ward Hill, MA, USA, technical grade, $P_2O_5 \leq 53$ wt %) stabilized by nitric acid («Reakhim», Samara, Russia, 70 wt %). The impregnated sample was dried at 110 °C for 4 h and calcined at 500 °C for 4 h. The obtained oxide precursor was reduced in hydrogen (flow rate = 150 mL/min per gram of precursor) at 600 °C (ramp = 1 °C/min) for 1 h and then cooled to room temperature. Finally, the sample was passivated in 1% O$_2$/He flow (flow rate = 80 mL/min) for 2 h at room temperature.

Ni/SiO$_2$ catalyst synthesis. The reference Ni/SiO$_2$ catalyst ($h$-Ni) was prepared by incipient wetness impregnating of silica granules with an aqueous solution of Ni(CH$_3$COO)$_2$$\cdot$4H$_2$O containing $2.1 \times 10^{-3}$ mol of Ni per gram of support, followed by drying at 110 °C for 4 h and then calcined at 500 °C for 4 h. The precursor was reduced by TPR in H$_2$ flow (flow rate = 60 mL/min) at 400 °C (ramp = 1 °C/min) for 4 h to obtain Ni/SiO$_2$ catalyst. Finally, the sample was passivated in 1% O$_2$/He flow (flow rate = 80 mL/min) for 2 h at room temperature.

The PO$_3$/SiO$_2$ ($h$-P$_{ox}$) reference sample was prepared by impregnating of silica with an aqueous solution of (NH$_4$)$_2$HPO$_4$ (4.2 $\times$ 10$^{-3}$ mol of P per gram of support), followed by drying at 110 °C for 4 h and calcination at 500 °C for 4 h Prior to use in hydrodeoxygenation, the precursor was activated by standard TPR procedure by heating in H$_2$ flow at 600 °C for 1 h.

3.2. Catalyst Characterization

The elemental analysis of the catalysts was performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 4300 DV (Perkin Elmer, Villebon-sur-Yvette, France).

The textural properties of the catalysts were determined using nitrogen physisorption at 77 K with an ASAP 2400 instrument (USA).

XRD measurements were performed on an X-ray diffractometer Bruker D8 Advance (Bruker, Karlsruhe, Germany) using CuK$_\alpha$ radiation (wavelength $\lambda$ = 1.5418 Å) in the 2θ scanning range of 10°–70°. The qualitative phase analysis was carried out using the JCPDS data base [46]. The quantitative phase analysis and refining of the unit cell parameters were carried out by Rietveld analysis of a diffraction pattern using X’Pert High Score Plus software. The average crystallite size ($D_{\text{XRD}}$) was calculated using the Scherrer equation applied to the (312) reflection at 2θ = 48.9° of Ni$_{12}$P$_5$ phase and to the (111) reflection at 2θ = 40.6° of Ni$_2$P phase correspondingly. The average crystallite size ($D_{\text{XRD}}$) of Ni$_{12}$P$_5$ nanoparticles was calculated using the Scherrer equation applied to the (312) reflection at 2θ = 48.9°.

The samples were investigated using high-resolution transmission electron microscopy with a JEM-2010 transmission electron microscope (JEOL, Tokyo, Japan) with accelerating voltage of 200 kV and resolution of 0.14 nm. The local elemental composition was analyzed with an energy-dispersive EDX spectrometer equipped with a Si(Li) detector (energy resolution—130 eV). To obtain statistical information, the structural parameters of ca. 500 particles were measured. To determine the mean particles diameter ($D_s$), the Sauter mean diameter was used calculated by the equation:

$$D_s = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$  \hspace{1cm} (2)

where $n_i$ is the number of particles, $d_i$ is the diameter of the $i$th particle.

The samples of the catalyst precursors were characterized by the H$_2$ temperature-programmed reduction method (H$_2$-TPR). An amount of 0.10 g of the calcined sample was loaded into a quartz U-tube reactor (inner diameter equal to 4 nm). The experiments were carried out in 10 vol % H$_2$/Ar flow (flow rate = 60 mL/min) at heating rate 10 °C/min in a temperature region from 80 to 900 °C.
The H$_2$ consumption was determined by a thermal conductivity detector (TCD). A cold trap (−60 °C) before the TCD was used in order to remove water from exhaust gas.

NMR experiments were carried out using a Bruker Avance-400 spectrometer at the resonance frequency of 161.923 MHz for $^{31}$P. Magic Angle Spinning (MAS) spectra were measured using a Bruker MAS NMR probe with 4-mm (outer diameter) ZrO$_2$ rotors at spinning frequency of 14 kHz. The $^{31}$P spectra were obtained using Hahn-echo sequence using a train of $\pi/2$-τ-$\pi$ pulses, the duration of $\pi/2$ was 2.4 µs. The interpulse delay τ was chosen with respect to the rotation frequency. The sequence repetition delay was 100 ms due to very short $^{31}$P relaxation time in Ni-P intermetallic compounds [47]. Due to very large spectra width, all spectra were collected by frequency stepped technique with a step of 600 ppm (with respect to $^{31}$P NMR frequency, ~100 kHz) covering ~5000–6000 ppm spectral width, the details can be found elsewhere [48]. The spectra were collected at room temperature and referenced to 85% water solution of orthophosphoric acid (for $^{31}$P experiments). The accuracy of the chemical shift was ±0.5 ppm. The number of transients was 16k in each frequency point. To avoid reduced catalyst oxidation by air, all samples were sealed in glass ampoules without oxygen access. Prior to NMR experiments, the catalysts were transferred from ampoule to NMR rotor in a glove box under argon atmosphere. This technique helps to minimize possible oxidation during NMR spectra acquisition.

3.3. Experimental Setup and Procedure

Methyl palmitate («Sigma-Aldrich», St. Louis, MO, USA, grade ≥ 97%), lauric acid («Sigma-Aldrich», St. Louis, MO, USA, grade ≥ 98%), dodecanol-1 («Sigma-Aldrich», St. Louis, MO, USA, grade ≥ 98%), n-dodecane («Acros Organics», New Jersey, USA, grade ≥ 99%) and n-octane («Kriokhrom», Saint Petersburg, Russia, grade ≥ 99.5%) were used for initial reaction mixtures preparation.

The catalytic activity in HDO of the methyl palmitate was evaluated in the trickle-bed reactor (inner diameter 9 mm and total length 265 mm) at the temperature 290 °C, hydrogen pressure 3.0 MPa, H$_2$/feed volume ratio 600 Nm$^3$/Nm$^3$, LHSV of MP was varied from 0.3 to 16 h$^{-1}$. The composition of the reaction mixture, wt %: methyl palmitate—10 (oxygen content—1.183 wt %), n-octane (used as an internal standard for quantification of liquid product)—2 and the rest—n-dodecane. The catalyst was placed in the middle part of the reactor between two layers of silicon carbide—inert material with high thermal conductivity, a layer of fine particles of catalyst diluted (0.2 ÷ 0.3 mm) silicon carbide in a ratio 1:4 to improve the wettability and uniformity of the liquid distribution in the catalyst layer, minimizing the effect of the wall surface and axial flow heterogeneity. Prior to the reaction, the passivated catalyst was re-reduced in situ in hydrogen (flow rate = 60 ml/min) at 400 °C and hydrogen pressure 5.0 MPa for 15 h. The liquid products were collected every hour till steady-state condition, and time on stream was not less than 8 h.

The conversion of methyl palmitate ($X_{MP}$), conversion of oxygen-containing compounds ($X_{OCC}$) and the selectivity to C$_{16}$ hydrocarbons ($S_{C_{16}}$) were calculated as follows:

$$X_{MP} = \left(1 - \frac{n_{MP}}{n_{MP}^*}\right) \times 100, \%$$  \hspace{1cm} (3)

$$X_{OCC} = \left(1 - \frac{n_{O}}{n_{O}^*}\right) \times 100, \%$$  \hspace{1cm} (4)

$$S_{C_{16}} = \left(\frac{n_{C_{16}}}{n_{MP} - n_{MP}^*}\right) \times 100, \%$$  \hspace{1cm} (5)

where $n_{MP}^*$ and $n_{MP}$ are the initial and the current methyl palmitate content in the reaction mixture expressed in mols, $n_{O}^*$ and $n_O$ are the initial and current oxygen content in the reaction mixture expressed in mols, $n_{C_{16}}$ is the amount of C$_{16}$ hydrocarbons in the products at $X_{MP} = 100\%$ expressed in mols.
The apparent catalytic activity \( A_{\text{HDO}} \) of the samples in methyl palmitate HDO was evaluated as follows:

\[
A_{\text{HDO}} = \frac{X_{\text{OCC}} \cdot F}{\omega_{\text{cat}} \cdot C_{\text{Ni}}} \quad \text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}
\]  

(6)

where \( X_{\text{OCC}} \) is the conversion of oxygen-containing compounds (\%), \( F \) is the molar rate of methyl palmitate fed into the reactor (mol·h\(^{-1}\)), \( \omega_{\text{cat}} \) is the catalyst weight (g) and \( C_{\text{Ni}} \) is the nickel content in the catalyst (wt %). \( A_{\text{HDO}} \) was calculated at the MP conversion below 20%.

The HDO activity (TOF) of the samples per metal site was estimated by the equation:

\[
\text{TOF} = \frac{X_{\text{MP}} \cdot F}{\omega_{\text{cat}} \cdot C_{\text{M.S.}}} \quad \text{s}^{-1}
\]  

(7)

where \( X_{\text{MP}} \) is the conversion of methyl palmitate (%), \( F \) is the molar rate of methyl palmitate (mol·s\(^{-1}\)), \( \omega_{\text{cat}} \) is the catalyst weight (g) and \( C_{\text{M.S.}} \) is the theoretical metal site concentration (mol·g\(^{-1}\)) calculated assuming cubic or spherical geometry of nickel phosphide particles uniformly distributed on the surface as follows:

\[
C_{\text{M.S.}} = \frac{6 \cdot \eta \cdot C_{\text{Ni}xP_y}}{\rho_{\text{Ni}xP_y} \cdot D_{\text{S}}} \quad \text{mol} \cdot \text{g}^{-1}
\]  

(8)

in which \( \eta \) is surface metal atom density, \( \rho_{\text{Ni}xP_y} \) is the bulk density of \( \text{Ni}_x\text{P}_y \) phase (Table 3) and \( D_{\text{S}} \) is the Sauter mean particles diameter obtained from TEM measurements, \( C_{\text{Ni}xP_y} \) is the fractional weight loading of nickel phosphide in the catalyst \( (\omega_{\text{Ni}xP_y}/\omega_{\text{cat}}) \). The theoretical metal atom site concentration is an approximate parameter.

### Table 3. Surface metal density and bulk density of nickel and nickel phosphide.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Surface Metal Density, % (Atoms·cm(^{-2}))</th>
<th>Compound Density, ( \rho ) (g·cm(^{-3}))</th>
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<tr>
<td>( \text{Ni}_2\text{P} )</td>
<td>1.01 \times 10^{15} [49]</td>
<td>7.35 [50]</td>
</tr>
<tr>
<td>( \text{Ni}_{12}\text{P}_5 )</td>
<td>1.21 \times 10^{15}</td>
<td>7.53 [50]</td>
</tr>
</tbody>
</table>

### 3.4. Products Analysis

The reaction products were identified using a GC/MS technique (Agilent Technologies 7000 GC/MS Triple QQQ GC System 7890A, Santa Clara, CA, USA) with a VF-5MS quartz capillary column (30 m × 0.25 mm × 0.25 μm). The liquid samples were analyzed with a gas chromatography system (Agilent 6890N, Santa Clara, CA, USA) equipped with HP-1MS column (30 m × 0.32 mm × 1.0 μm) and flame ionization detector (FID). Gaseous phase products were analyzed online with a gas chromatograph (Chromos 1000, Dzerzhinsk, Russia) equipped with a column packed with 80/100 mesh HayeSep\(^\text{®}\) (Sigma-Aldrich, St. Louis, MO, USA) and FID. The concentrations of CO and CO\(_2\) were analyzed in the form of methane after methanation over reduced Pd catalyst at 340 °C. The carbon balance across the reactor for all experiments was >95%.

The total oxygen content in the reaction mixture was determined using CHNSO elemental analyzer Vario EL Cube (Elementar Analysensysteme GmbH, Hanau, Germany).

### 4. Conclusions

To get a deeper insight into the Ni/P effect on the catalytic properties of silica-supported nickel phosphide catalyst in the aliphatic ester HDO two sets of the \( \text{Ni}_x\text{P}_y/\text{SiO}_2 \) catalysts differing in nickel content were prepared. Both high-loaded and low-loaded set of catalysts contain the samples with the initial Ni/P ratios adjusted to 2/1, 1/1 and 1/2. Set of high-loaded samples \( (h-\text{Ni}_x\text{P}_y/\text{SiO}_2) \) provides a reliable insight into the evolution of the active phase with the Ni/P decrease, while the set of low-loaded samples \( (l-\text{Ni}_x\text{P}_y/\text{SiO}_2) \) is an appropriate candidate for comparing catalytic behavior.
in the terms of TOF due to the similar value of the mean particle sizes in the catalysts with different Ni/P values.

Summarizing the XRD, TEM and NMR results of catalysts characterization it was concluded that the initial Ni/P molar ratio influences phase composition of the reduced phosphide catalysts: Ni$_2$P produced using the initial Ni/P molar ratio of 1 and 0.5, while the initial Ni/P molar ratio of 2 favors formation of Ni$_{12}$P$_5$ phase. According to TEM data have shown the high-loaded samples ($h$-Ni$_2$P$_1$, $h$-Ni$_1$P$_1$, and $h$-Ni$_1$P$_2$) was shown with TEM contain phosphide particles with the broad particle size distribution (from 2 to 20 nm), while uniformly distributed phosphide particles with the mean particle diameter 4.9 nm for $l$-Ni$_2$P$_1$, 4.7 nm for $l$-Ni$_1$P$_1$ and 3.5 nm for $l$-Ni$_1$P$_2$ were observed. $^{31}$P MAS NMR results showed that an increase of Ni/P ratio is accompanied by the increase of the PO$_x$ groups on the surface of high-loaded samples; the same dependence was speculated for the low-loading samples taking into account the similarities in the active phase composition and TPR behavior.

Catalytic activity in methyl palmitate HDO normalized to metal content was found to increase with the decrease of Ni/P content in the catalysts and such dependence was true for both sets of catalysts. The same trend of TOF increase over the $l$-Ni$_x$P$_y$/SiO$_2$ catalysts was explained by the acceleration of methyl palmitate transformation due to the hydrolysis of methyl palmitate over acid PO$_x$ groups of the nickel phosphide catalysts. The obtained dependence corroborates our previous results, where the increase of phosphate groups content through the adjusting of phosphorus precursor and reduction temperature provides the increase of methyl palmitate conversion rate in HDO [15].

The decrease of Ni/P ratio in the silica-supported nickel phosphide catalysts was shown to increase the rate of methyl palmitate conversion most probably through the hydrolysis of methyl palmitate over acid sites presented by the phosphate groups of the silica-supported nickel phosphide catalysts. Thus, the employment of support with the pronounced acidity for the preparation of supported phosphide catalysts can significantly increase the rate of fatty ether HDO and alkane production. However, the appropriate balance of acid and metal functionalities is crucial to provide the high catalytic activity of phosphide catalysts in the overall reaction of methyl palmitate HDO, comprising the variety of acid-catalyzed and metal-catalyzed reactions.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/10/298/s1. Figure S1: TEM images of Ni$_x$P$_y$/SiO$_2$ catalysts with different initial molar Ni/P ratio: (a) $l$-Ni$_2$P$_1$; (b) $l$-Ni$_1$P$_1$; (c) $l$-Ni$_1$P$_2$, Figure S2: $H_2$-TPR profiles of Ni$_x$P$_y$/SiO$_2$ catalyst oxide precursors with different nickel phosphide loading: $h$-Ni$_2$P$_1$ and $l$-Ni$_1$P$_2$, Figure S3: Effect of the dodecanol additive on methyl palmitate conversion during HDO over $l$-Ni$_1$P$_2$ catalyst. Feed composition: mixture 1–10.0 wt % MP in n-octane; mixture 2–10.0 wt % MP and 5 wt % C$_{12}$H$_{25}$OH in n-octane. Reaction conditions: $P_{H_2}$ = 3.0 MPa, $T$ = 290 °C, $H_2$/feed = 600 Nm$^3$/Nm$^3$, LHSV of $MP$ = 1.02 h$^{-1}$, Figure S4: n-Pentadecane concentration in liquid phase versus CO concentration in exhaust gas phase during palmitic acid HDO over $l$-Ni$_1$P$_2$ catalyst. Reaction conditions: feed composition 5.0 wt % palmitic acid in n-dodecane, $P_{H_2}$ = 3.0 MPa, $T$ = 290 °C, $H_2$/feed = 600 Nm$^3$/Nm$^3$, LHSV = 0.3–6.4 h$^{-1}$, Figure S5: Methyl palmitate and oxygen-containing compounds conversions and C$_{16}$ hydrocarbons selectivity (S$_{C_{16}}$) during methyl palmitate HDO over $h$-Ni$_1$P$_2$ catalysts. Reaction conditions: $P_{H_2}$ = 3.0 MPa, $T$ = 290 °C, $H_2$/feed = 600 Nm$^3$/Nm$^3$, LHSV = 10.7 h$^{-1}$.

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Author Contributions: G.A.B. conceived and designed the experiments and supervised the work; I.V.S. performed the catalyst synthesis; I.V.D., I.V.S. and P.V.A. performed the catalytic activity tests; E.Y.G. performed the catalyst characterization by TEM; V.P.P. performed the catalyst characterization by XRD; I.V.Y. and O.B.L. performed the catalyst characterization by MAS NMR; I.V.D., P.V.A., I.V.S. and G.A.B. analyzed the experimental data and wrote the paper.

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