Hydrodeoxygination of Methyl Palmitate over Supported Ni Catalysts for Diesel-like Fuel Production

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ABSTRACT: Catalytic hydrodeoxygenation (HDO) of vegetable oils to renewable alkane-type biofuels has attracted more and more concern in recent years. However, the presently used catalysts were mainly focused on the sulfided CoMo and NiMo catalysts, which inevitably posed sulfur contamination in final products. Therefore, exploring nonsulfured catalyst for this processing is of fundamental importance, but it is still an open challenge. In this paper, we prepared the sulfur free Ni supported on SiO2, γ-Al2O3, SAPO-11, HZSM-5, and HY by incipient wetness impregnation and tested the catalytic performance in HDO of methyl palmitate. Alkanes with long carbon chains were mainly produced with two possibly parallel approaches: hydrogenation of hexadecanal to hexadecanol, followed by dehydration/hydrogenation to C16 alkane and decarbonylation/decarboxylation of hexadecanoic acid to C15 alkane. The acidity of catalysts significantly influenced their catalytic performance, and the Ni/SAPO-11 catalysts with weak and medium acidity showed superior properties to the other catalysts due to the synergetic effect of metal Ni and acidic support. The maximum yield of 93% for C15+ alkanes was observed over 7 wt % Ni/SAPO-11 under the mild reaction conditions of 493 K and 2 MPa, indicating its promising application in this reaction.

1. INTRODUCTION

Fast development of modern industry and continued depletion of fossil energy entailed significant environment pollution and greenhouse CO2 emission, which forces researchers worldwide to focus their vision on renewable energy for substituting the present fossil fuels. Of those renewable fuels, biofuel has received significant interest in the past decade because it presents as a unique carbon included fuel that is favorable for transportation.1,2 Currently, biodiesel produced by transesterification of vegetable oils and methanol is widely used as a renewable fuel.3–9 However, biodiesel usually suffers from disadvantageous fuel properties such as relatively high freezing point due to the involved oxygen atoms, and limited compatibility with gas engines, low chemical stability, and low caloric value due to the involved oxygen atoms and the unsaturated C–C bonds, as comparing with the present fossil fuels.10–13 In order to overcome these disadvantages of biodiesel, catalytic hydrodeoxygenation (HDO, the essential removal of oxygen atoms and saturation of unsaturated C–C bonds) of biomass derived fatty acids14,15 aliphatic esters1,16–18 and/or vegetable oils19–21 for the production of diesel-like hydrocarbon fuels has been intensively investigated in recent years.

The primary HDO catalysts were mainly dispersed on noble metals Pt,11 Pd,14 and transition metals Ni–Mo, Co–Mo, and Ni–W on the supports of γ-Al2O3,16–18 activation carbon,14 SiO2,21 and SBA-15,15 etc. Noble metals showed high activity and stability, but their extortionate cost limits their essential application on a large scale. On the other hand, the transition metals Ni and Co with promoters of Mo or W were comparable to the noble metals. NiMo/γ-Al2O3 and CoMo/γ-Al2O3 catalysts were widely used in HDO of vegetable oils for producing high yield of hydrocarbon fuels,16–18 and the HDO mechanism investigation revealed that HDO of vegetable oils is a multistep reaction with oxygen-containing compounds including aliphatic alcohols and fatty acids as the intermediates.22,23 Aside from the above-mentioned HDO pathway, decarbonylation and/or decarboxylation also occurred parallel with obtaining the main products of aliphatic chain length hydrocarbons containing one less carbon than the correspondent feedstocks.15 It is noted that although these modified transition metals showed a highly catalytic performance in this kind of HDO reaction, the introduction of sulfur containing agents is necessary to keep the sulfided state of catalysts during catalyst pretreatment and HDO processing, which inevitably brings about sulfur pollution in the final products. For example, a previous report testified that the maximum molar concentration of heptanethiol in the liquid products was 0.4% with 400 ppm of H2S addition, during HDO of methyl heptanoate over the sulfided NiMo/γ-Al2O3 catalysts.24 Therefore, exploring nonsulfided metal catalyst for avoiding such drawbacks is of fundamental importance, but it still an open challenge.

It is well-known that the exposed acid/base sites of the catalyst support could also participate in the activation of reactants and play the essential role in governing product distribution. For example, significantly increased cracking C1–C4 alkanes, aromatization arenes, and severe carbon deposition were observed with using strong acidic HZSM-5 zeolite as catalyst.25 Comparatively, over basic MgO, the heavy alkanes with carbon number of more than 35 were mainly manufactured due to C–C coupling of fatty ester intermedi-
In this work, we prepared Ni supported on γ-Al₂O₃, SiO₂, HY, HZSM-5, and silicaluminoorthophosphate-11 (SAPO-11) catalysts by initial wetness impregnation and compared their catalytic performance in HDO of methyl palmitate (the model compound of vegetable oil) to diesel like fuel. The physicochemical properties of catalysts were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), thermogravimetric (TG), NH₃-temperature-programmed desorption (NH₃-TPD), H₂-temperature-programmed reduction (H₂-TPR), and H₂-chemisorption techniques, and the possible HDO reaction pathway was proposed.

2. EXPERIMENTAL SECTION

2.1. Materials. Five kinds of support materials γ-Al₂O₃, SiO₂, and HY (Si/Al = 2.91), HZSM-5 (Si/Al = 38), and SAPO-11 (Si/Al = 0.11 and Al/P = 1) zeolites were commercially purchased from Tianjin Chemical Scientific Co. Ltd. Methyl palmitate (Aladdin, purity > 98%), analytic graded Ni(NO₃)₂·6H₂O and cyclohexane were provided by Tianjin Fuyu Fine Chemical Co., Ltd. and used without further purification.

2.2. Catalyst Preparation and Characterization. All the Ni-based catalysts were prepared by impregnating the catalyst support in aqueous solution of Ni(NO₃)₂·6H₂O with the desired Ni loading. The resultant suspension was stirred for 10 h at ambient temperature, followed by evaporating excess water at 353 K. The solids remained were dried at 393 K and calcined at 823 K for 3 h in air. The catalysts were reduced at 773 K for 3 h under 5 vol. % H₂/N₂ flow before use.

XRD patterns of the catalysts were obtained with using x-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), thermogravimetric (TG), NH₃-temperature-programmed desorption (NH₃-TPD), H₂-temperature-programmed reduction (H₂-TPR), and H₂-chemisorption techniques, and the possible HDO reaction pathway was proposed.

2.3. Catalytic Performance. HDO of methyl palmitate was carried out in a 100 mL semibatch stainless autoclave furnished with a mechanical stirrer and a condensing tube cooled by flowing ice-cooled water at export. In a typical reaction, 1.0 g freshly reduced catalyst and 300 g methyl palmitate were loaded in the autoclave. After removing air in the reactor with argon flushing, H₂ was introduced and pressurized at 2 MPa by pressure regulating valves. The H₂ flow was controlled at 50 mL/min. The reaction system was then heated to 493 K and maintained at this temperature for 360 min. During the reaction, the stirring speed was maintained at 1000 rpm to prevent external mass transfer limitation and the gas products were collected at every 30 min.

2.4. Product Analysis. C₅−C₁₄ hydrocarbons and dimethyl ester (DME) were analyzed by a GC 9800 chromatography equipped with a flame ionization detector (FID) and a packed column (Porapak-Q column, 3 m × 3 mm) by using nitrogen as carrier gas, and CO, CO₂, and CH₄ was analyzed by another GC 9800 equipped with a TCD and a packed column (TDX-01 column, 3 m × 3 mm) with using helium as carrier gas. All of the gas products were quantified by external standard method with using the peak area of CH₄ as correlation.

The liquid products were collected with cyclohexane, identified by GC-MS measurement, and quantified by an Agilent Technologies 4890 gas chromatography equipped with a capillary column (DB-1701, 60 m × 0.25 mm ×0.25 μm) and FID by using n-nonadecane as the internal standard. Conversion of methyl palmitate (Xₐ) and selectivity of product i (Sᵢ) were defined as

\[ Xₐ (\%) = \frac{wᵢ₀ - wᵢ}{wᵢ₀} \times 100 \]

\[ Sᵢ (mol \%) = \frac{nᵢ × aᵢ}{\sum nᵢ × aᵢ} \times 100 \]

Here, wᵢ₀ refers to the initial weight of methyl palmitate, and wᵢ is the weight of final methyl palmitate after reaction; nᵢ indicates the moles of product i, and aᵢ represents the carbon atom number of product i.

3. RESULTS AND DISCUSSION

3.1. HDO of Methyl Palmitate. The catalytic performance of Ni catalysts with different supports was compared in HDO...
of methyl palmitate under the mild reaction condition of 493 K, 2 MPa of H₂ pressure and 360 min, and the results were listed in Table 1. For all catalysts, the primary products were mainly composed of the gaseous CO, CO₂, dimethyl ether (DME, produced by methanol dehydration) and C₁−C₄ alkanes, the liquid palmitic acid and alkanes with the carbon numbers of more than 5, and the hexadecanal, hexadecanol, and hexadecene intermediates with trace amounts of less than 0.01% (the data are not shown here). Over 7 wt % Ni/SiO₂, the relatively low methyl palmitate conversion and the selectivity to liquid alkane products presented as 49.3% and 90.7%, respectively. Among those products, pentadecane was confirmed as the highest selectivity of 61% with medium amounts of cracking C₁−C₄ and C₅−C₁₄, and coupling C₁₆+ alkanes. For the 7 wt % Ni/HZSM-5 and 7 wt % Ni/HY catalysts, although the conversions of methyl palmitate were drastically increased to nearly 100%, the target liquid alkanes significantly declined to 63% over 7 wt % Ni/HZSM-5 and 53% over 7 wt % Ni/HY, owing to the obviously incremental selectivities of the unwanted cracking C₁−C₄ alkanes. Comparatively, both 7 wt % Ni/γ-Al₂O₃ and 7 wt % Ni/SAPO-11 presented the high methyl palmitate conversions which were similar to 7 wt % Ni/SiO₂ and 7 wt % Ni/HY and the high selectivities of liquid alkane products which were resembled to 7 wt % Ni/SiO₂, indicating the superior catalytic performance in HDO of methyl palmitate. For instance, the maximal 99.8% of methyl palmitate conversion and 95.8% of selectivity for the target liquid alkanes were obtained over 7 wt % Ni/SAPO-11. Apart from 7 wt % Ni/γ-Al₂O₃, the Ni based catalysts showed isomerization activity in HDO of methyl palmitate under the given reaction condition, but all the selectivities was less than 2%.

Taking into account that the Ni supported on SAPO-11 showed the best catalytic performance in HDO of methyl palmitate, we further evaluated the properties of Ni/SAPO-11 catalysts with different Ni loadings and the results were summarized in Table 2. As Ni loadings increased from 2 wt % to 7 wt %, conversions of methyl palmitate monotonously increased from 60% to 99.8%, respectively. The selectivities to the liquid alkanes of C₅+ also slightly increased from 93.4% to 95.8%. Comparatively, as the Ni loading was further increased to 9 wt %, both the conversion of methyl palmitate and the selectivity of C₅+ alkanes kept almost unchanged. For all Ni/SAPO-11 catalysts, the total selectivities of 83−90% for C₁₅ and C₁₆ alkanes observed with the relatively low C₁₅/C₁₆ ratios and the cracking products were controlled at very low levels.

![XRD patterns](image)

**Figure 1.** XRD patterns of the supported Ni catalysts (A) for (a) 7 wt % Ni/SiO₂, (b) 7 wt % Ni/γ-Al₂O₃, (c) 7 wt % Ni/SAPO-11, (d) 7 wt % Ni/HY, and (e) 7 wt % Ni/HZSM-5 and the Ni/SAPO-11 catalysts (B) for (a) SAPO-11, (b) 2 wt % Ni/SAPO-11, (c) 5 wt % Ni/SAPO-11, (d) 7 wt % Ni/SAPO-11, and (e) 9 wt % Ni/SAPO-11.

**Table 2.** HDO of Methyl Palmitate over Ni/SAPO-11 Catalysts’

<table>
<thead>
<tr>
<th>catalyst</th>
<th>conversion (%)</th>
<th>DME</th>
<th>CO</th>
<th>CO₂</th>
<th>C₅−C₄</th>
<th>i⁻n⁻</th>
<th>n⁻/i⁻</th>
<th>C₁₅</th>
<th>C₁₆</th>
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<tr>
<td>2 wt % Ni/SAPO-11</td>
<td>60.0</td>
<td>4.38</td>
<td>1.33</td>
<td>0.00</td>
<td>0.84</td>
<td>0.00</td>
<td>1.05</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>5 wt % Ni/SAPO-11</td>
<td>93.0</td>
<td>1.58</td>
<td>1.54</td>
<td>0.00</td>
<td>3.20</td>
<td>2.35</td>
<td>0.00</td>
<td>0.00</td>
<td>0.67</td>
</tr>
<tr>
<td>7 wt % Ni/SAPO-11</td>
<td>99.8</td>
<td>1.12</td>
<td>0.83</td>
<td>0.01</td>
<td>2.21</td>
<td>2.60</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9 wt % Ni/SAPO-11</td>
<td>99.2</td>
<td>1.30</td>
<td>1.36</td>
<td>0.04</td>
<td>2.88</td>
<td>2.96</td>
<td>0.00</td>
<td>0.00</td>
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</table>

*Reaction conditions: T = 493 K, P = 2.0 MPa, t = 360 min. i⁻ for isoalkanes. n⁻ for normal alkanes.

**Table 3.** HDO of Methyl Palmitate over 7 wt % Ni/SAPO-11 Catalyst at Different Reaction Times”

<table>
<thead>
<tr>
<th>reaction time (min)</th>
<th>conversion (%)</th>
<th>DME</th>
<th>CO</th>
<th>CO₂</th>
<th>C₅−C₄</th>
<th>i⁻n⁻</th>
<th>n⁻/i⁻</th>
<th>C₁₅</th>
<th>C₁₆</th>
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<tr>
<td>180</td>
<td>48.7</td>
<td>1.38</td>
<td>1.12</td>
<td>0.65</td>
<td>0.01</td>
<td>3.39</td>
<td>0.00</td>
<td>0.16</td>
<td>0.00</td>
</tr>
<tr>
<td>360</td>
<td>99.8</td>
<td>1.12</td>
<td>0.83</td>
<td>0.01</td>
<td>2.21</td>
<td>2.00</td>
<td>0.47</td>
<td>18.1</td>
<td>47.45</td>
</tr>
</tbody>
</table>

*Reaction conditions: T = 493 K, P = 2.0 MPa. i⁻ for isoalkanes. n⁻ for normal alkanes.
Additionally, the selectivities to isoalkanes slightly increased as the Ni loadings increased from 2 wt % to 7 wt %.

The influence of reaction time on the catalytic performance of 7 wt % Ni/SAPO-11 catalyst was shown in Table 3. As reaction time increased, the conversion of methyl palmitate rose significantly and 99.8% of conversion was obtained at 360 min, indicating that methyl palmitate was nearly completely transformed. The reaction time also significantly influenced the production selectivities in HDO of methyl palmitate. At the reaction time of 180 min, the percentages of C5+ liquid alkanes and palmitic acid were 25.7% and 58.75%, respectively. When the reaction time was extended to 360 min, none of palmitic acid was detected and the selectivity to the liquid alkanes drastically raised to 95.8%, showing that palmitic acid act as an intermediate and convert into the downstream alkanes during this HDO process. This is well consistent with the previous reports.22,23 It is noted that CH4, which is produced by the hydrogenolysis of methyl palmitate and/or the hydrogenation of the primary CO/CO2 and methanol, was detected as the percentages of more than 90% in the gas hydrocarbon products independent of the reaction time (the data are not shown here).

3.1. Catalyst Characterization. The XRD patterns of the 7 wt % Ni based catalysts with different supports were shown in Figure 1A. The characteristic diffractions associated to the supports of γ-Al2O3, SAPO-11, HZSM-5 and HY were presented, indicating that the structures of the employed supports could be largely kept as 7 wt % Ni was impregnated and calcined. Over 7 wt % Ni/SAPO-11, 7 wt % Ni/HZSM-5, and 7 wt % Ni/HY, the characteristic diffraction peaks were clearly observed at 2θ = 44.5°, 51.8°, and 76.4°, corresponding to the (111), (200), and (220) crystallographic planes of face-centered cubic Ni phase, respectively. This demonstrated that only small amounts of Ni could be accommodated in the micropores of SAPO-11, HZSM-5, and HY, the remaining ones aggregating on the external surface of the supports to form particles. Although amorphous SiO2 generally shows the large surface area, pore sizes, and volume, the Ni phase was also observed as the obvious diffractions, which is possibly due to the weak interactions between the Ni species and SiO2 surface and leads to significant aggregation in the pore wall of SiO2. On the other hand, no characteristic diffractions relative to Ni were observed over 7 wt % Ni/γ-Al2O3, indicating that the Ni species can be highly dispersed on the surface of γ-Al2O3, with their sizes below the detective limitation of the XRD instrument. In addition, characteristic diffraction peaks of NiO (2θ = 37.3°, 43.2°, and 62.8°) were observed with low intensities over 7 wt % Ni/SAPO-11, 7 wt % Ni/HZSM-5, and 7 wt % Ni/HY, which indicates that the supported Ni2+ species could not be fully reduced to the metallic state under the given pretreatment condition due to the strong interactions of partial Ni2+ species and the supports.

Figure 1B showed the XRD patterns of Ni/SAPO-11 catalysts with different Ni loadings. Diffractive peaks of SAPO-11 could be seen in all diffraction profiles, indicating that the structure of SAPO-11 was largely retained after impregnation and calcination. When the Ni loadings were no more than 2 wt %, the absence of the characteristic diffraction peaks relative to Ni phase indicated the high dispersion of Ni species on SAPO-11 surface, possibly due to some of Ni species being diffused into the microchannels of SAPO-11. As the Ni loadings increased to 5 wt % and above, the diffractions corresponding to NiO and Ni crystallographic phase occurred and their intensities raised with increasing the Ni loadings, which demonstrated that the excessive amounts of Ni deposited...
on the external surface of SAPO-11 and agglomerated into larger particles.

Figure 2 showed the SEM images of the pristine SAPO-11, and the fresh and spent 7 wt % Ni/SAPO-11 catalysts. The pure SAPO-11 presented as a relatively smooth surface with the size of several micrometers. For the fresh 7 wt % Ni/SAPO-11, the support sizes kept almost unchanged and the sizes of the NiO particles were 30–100 nm. The SEM image with a larger magnification (Figure 2c) showed that the NiO particles exclusively presented as the sharp-edged octahedral shape with one side attached to the surface of support and the others exposing to the air. The SEM image of the spent 7 wt % Ni/SAPO-11 was shown in Figure 2d. Despite reduction to the metallic state by H2 and survival from HDO of methyl palmitate, the Ni particles presented as nonaggregation and their original octahedrons transferred to the spheres with the sizes of 20–80 nm, showing the stability of this catalyst in HDO of methyl palmitate.

Table 4 shows the textural properties and H2-chemisorption of Ni based catalysts with different supports. The catalyst 7 wt % Ni/SiO2 had the largest surface area, with the external surface of 120.7 m2/g, indicating that its surface area was mainly contributed by the internal micropores of HY. This was similar to 7 wt % Ni/γ-Al2O3 catalyst, which possessed the total and external surface area of 173.3 m2/g and 85.6 m2/g, respectively. For the 7 wt % Ni/SAPO-11 catalyst, the surface area was 33.5 m2/g with the external surface area of 33.0 m2/g, which is possibly due to the supported Ni particles blocking the micropores of SAPO-11 and creating the external surface of 7 wt % Ni/SAPO-11 by Ni particles themselves. Both 7 wt % Ni/SiO2 and 7 wt % Ni/γ-Al2O3 presented large surface areas, pore sizes, and volumes, which is ascribed to the fact that the larger pore sizes and volumes of SiO2 and γ-Al2O3 could accommodate enough Ni particles and no pore blockage occurred. To estimate the dispersions of Ni particles and their sizes, H2-chemisorption experiments were implemented, and the results were listed in Table 4. Dependent on the support used, the dispersion of Ni particles were 5.1%, 3.8%, and 3.0% and the Ni particle sizes were estimated as 20 nm, 27 nm, and 34 nm over HZSM-5, γ-Al2O3, and SAPO-11, respectively, according to the previous calculation.26 The Ni particle sizes determined by H2-chemisorption are well consistent with the SEM results (Figure 2d). For supported Ni catalysts, the dispersion of Ni particles is dependent on the textual and surface properties of supports, and those with large surface areas, pore sizes, and volumes, and strong interactions with Ni2+ species facilitated dispersing Ni particles and obtaining the smaller Ni particle sizes. Thus, it is rational that 7 wt % Ni/HZSM-5 and 7 wt % Ni/SiO2 presented relatively higher Ni dispersions than 7 wt % Ni/SAPO-11.

Textural properties of Ni/SAPO-11 catalysts were shown in Table 5. The original SAPO-11 presented the total surface area of 86 m2/g with the minor partition of external surface of 30 m2/g (created by SAPO-11 particles), which reflected the essential contribution of micropores in surface area of SAPO-11. As Ni was loaded and increased, the total surfaces of the Ni/SAPO-11 catalysts significantly dropped and stabilized at about 33 m2/g, with the exclusively external surface remaining. On the other hand, the mesoporous volumes (Table 5) and the pore size distributions (Figure 3) of the Ni/SAPO-11 samples gradually declined from 0.096 cm3/g and 10 nm for the pristine SAPO-11 to 0.078 cm3/g and 8 nm for 9 wt % Ni/SAPO-11, respectively. SAPO-11, which possesses one-dimensional micropore size of elliptical 0.39 nm ×0.63 nm with a 10-member ring, was first synthesized by substituting Si for P or Al and P in the parent aluminophosphate framework in 1984.29 It is more likely that such small pore sizes of SAPO-11 could not afford enough space to accommodate the Ni species, even at the low Ni loading of 2 wt %, which inevitably leads to part of Ni species located on the pore mouth and blocks the microchannels, inducing a significant decrease of microporous surface. As Ni loadings increased, the excessive Ni stacks on the external surface of the support and grows into larger particles, resulting in the mesoporous volumes and pore sizes of the Ni/SAPO-11 catalysts decreasing gradually.
Figure 4A showed the H₂-TPR profiles of the Ni based catalysts with different supports. Over 7 wt % Ni/HZSM-5 and 7 wt % Ni/SiO₂, the single H₂-consumption peaks were observed at 690 K for HZSM-5 and at 665 K for SiO₂, indicating the reduction of bulky NiO due to the weak interaction between Ni²⁺ and supports. For 7 wt % Ni/SAPO-11, two reduction peaks presented at 725 and 870 K, showing that two distinct Ni²⁺ species of easily reduced and relatively hardly reduced simultaneously existed on the surface of SAPO-11. Comparatively, 7 wt % Ni/γ-Al₂O₃ presented three superimposed reduction peaks at the low temperature of 760 K, the medium temperature of 920 K, and the high temperature of 1050 K, which is probably responsible for the reduction of the bulk or free NiO phase; the Ni²⁺ species directly bonded to γ-Al₂O₃ via bridged oxygen atoms and the incorporated Ni²⁺ of spinel NiAl₂O₆, respectively. On the other hand, 7 wt % Ni/HY showed the similar three reduction peaks but with the peaks at the low and the medium temperature shifting to 625 and 815 K, respectively, and keeping the peak at the high temperature almost unchanged. In terms of the previous report, the peak at the medium temperature is attributed to the reduction of the Ni²⁺ localized in the supercage and/or sodalite cavities, while the peak at the high temperature is due to the reduction of the Ni²⁺ localized in the hexagonal cavities.

Figure 5. NH₃-TPD profiles for (A) the supported Ni catalysts, (a) 7 wt % Ni/SiO₂, (b) 7 wt % Ni/SAPO-11, (c) 7 wt % Ni/γ-Al₂O₃, (d) 7 wt % Ni/HZSM-5, and (e) 7 wt % Ni/HY and (B) the Ni/SAPO-11 catalysts, (a) SAPO-11, (b) 2 wt % Ni/SAPO-11, (c) 5 wt % Ni/SAPO-11, (d) 7 wt % Ni/SAPO-11, and (e) 9 wt % Ni/SAPO-11.
leading to the latter Ni\textsuperscript{2+} species reduced at higher temperatures.\textsuperscript{31,33} In the present cases, the Ni\textsuperscript{2+} species at low loadings could highly disperse on SAPO-11 surface, with most directly combining to the support and hardly reduced by H\textsubscript{2}, bringing about their reduction peaks located at higher temperatures, while more bulky NiO particles produced at the incremental Ni loadings, thus shifting the corresponding reduction peaks to the declined temperatures. These Ni\textsuperscript{2+} species with strongly interacted with SAPO-11 act as a binding to fix the metallic Ni particles from coalescence during HDO of methyl palmitate.

Figure 5A showed the NH\textsubscript{3}-TPD profiles of the Ni based catalysts with different supports. In the spectra of 7 wt % Ni/SiO\textsubscript{2} catalyst, only a small hump centered at 470 K was observed, showing that this catalyst presented the very weak acidity and small acidic sites. For 7 wt % Ni/\gamma-Al\textsubscript{2}O\textsubscript{3}, two broad NH\textsubscript{3} desorption peaks appeared at about 515 and 607 K, assigning to the weak and medium acidic sites, respectively, which was well consistent with the previous report.\textsuperscript{34} For 7 wt % Ni/SAPO-11, the NH\textsubscript{3} desorption peak location of low temperature was at 470 K with a broad shoulder centered at 586 K, demonstrating that both the weak and the medium acidic sites presented simultaneously on this catalyst surface. According to the previous report, these weak acidic sites were possibly characterized as Brønsted or Lewis type, while the medium ones at relatively high temperature corresponded to the Bronsted sites, which originated from incorporation of Si into the framework of AlPO\textsubscript{4} for replacing P.\textsuperscript{35} Using zeolite HY as the support, the NH\textsubscript{3} desorption peak was mainly presented at 502 K with an additional small hump at about 795 K, evidencing that both the weak and the strong acidic sites appeared with the weak acidity as the majority. It is highly possible that this large amount of acidic sites is attributed to the high Al content in HY zeolite (Si/Al = 2.91). As for 7 wt % Ni/HZSM-5, three distinct NH\textsubscript{3} desorption peaks corresponding to weak and strong acidic sites appeared at 500, 690, and 775 K, respectively, and the peak area of strong acidity is comparable to that of the weak one.

The NH\textsubscript{3}-TPD profiles of Ni/SAPO-11 catalysts with different Ni loadings were shown in Figure 5B. As compared to the pristine SAPO-11, the total acidic amounts of the Ni/SAPO-11 catalysts decreased gradually, while with the medium acidic sites significantly increased. This drop of total acidic sites is possibly ascribed to the inaccessibility of SAPO-11 microchannels, which are impeded by Ni impregnation. On the other hand, those increased medium acidic sites over the Ni/SAPO-11 catalysts seem to be generated by the supported Ni particles, as indicated by the previous report.\textsuperscript{36}

3.3. Discussion. HDO of vegetable oils usually presented a complicated reaction network of parallel and/or consecutive hydrogenation, decarboxylation/decarbonylation, dehydrogenation, cracking, and carbon deposition, which involved the oxygenates such as methanol, hexadecanoic acid, hexadecanial, and hexadecanol as the intermediates and CO\textsubscript{2}, CO, and alkanes as the final products.\textsuperscript{18,23,37,38} As shown in Scheme 1, alkanes with long chains are mainly produced by the following two distinct approaches. The hexadecane intermediate is produced by hydrogenolysis of methyl palmitate, and further hydrogenated to C\textsubscript{16} alkane through hexadecanol and hexadecene (dehydration of hexadecanol). Due to the very fast transformation for the aldehyde hydrogenation, the alcohol dehydrogenation and the corresponding hexadecene hydrogenation, these intermediates were detected as trace amounts in the final products (all the contents were less than 0.01\%). On the other hand, hexadecanoic acid intermediate, which is produced by an alternative hydrogenolysis of methyl palmitate, could be decarbonylized/decarboxylized to C\textsubscript{15} alkane with CO/CO\textsubscript{2} as the byproducts or directly hydrogenated to C\textsubscript{16} alkane via hexanal, hexanol, and hexadecene as the sequential intermediates. Both C\textsubscript{15} and C\textsubscript{16} alkane could be cracked into the light alkanes over acidic catalysts. Considering H\textsubscript{2}O formed from methanol and hexadecanol dehydrogenation, hexadecanoic acid intermediate could be also produced by methyl palmitate hydrolysis. It is noted that although the decarbonylation/decarboxylation approach is proposed based on hexadecanoic acid intermediate, the similar transformation might also occur over methyl palmitate feedstock because of their similar molecular structure.

HDO of methyl palmitate (Table 1) showed that the acidity of the catalysts significantly promoted conversion of methyl palmitate and tailored the product distribution. With aiming to yield higher liquid alkanes, the catalysts (such as 8-Al\textsubscript{2}O\textsubscript{3} and SAPO-11) with relatively small acidic sites and simultaneously presented weak and medium acidity are appropriate. For these bifunctional catalysts, the acidity promoted effect could be supposed that the electrophilic acidic sites of catalyst surface activate the carbonyl and/or bridge oxygen atoms of methyl palmitate, weakening the acyl and/or ether bond, which is favorable to be attacked by the over spilled H atoms activated from the adjacent Ni.\textsuperscript{39} This results in the formation of 1-hexadecanal and methanol by the acyl bond activation and/or hexadecanoic acid and methane by the ether bond activation, both of which are followed by hydrodeoxygenation and/or decarbonylation/decarboxylation to the final C\textsubscript{15} and C\textsubscript{16} alkanes. Furthermore, acidic function of catalysts could also mediate product selectivity via controlling competitive hydrogenation and decarbonylation/decarboxylation during HDO of methyl palmitate. Over 7 wt % Ni/SiO\textsubscript{2} with weak acidity, the abundant C\textsubscript{15} alkane and the high ratio of C\textsubscript{15} to C\textsubscript{16} mean that
HDO of methyl palmitate basically proceed as the manner of decarbonylation/decarboxylation due to the dominant metal Ni effect.40 As medium acidity introduced, the selectivities of C16 alkane significantly enhanced due to its promotion effect via hydrogenation. The comparable contents for C15 and C16 alkanes indicate the balance of the acidity and metal of Ni/SAPO-11 catalysts employed (Table 2). However, the strong acidity posed the significantly incremental selectivities of the gaseous C1−C4 alkanes at the expense of those for C15 and C16 alkanes, indicating the severe cracking of the produced long chain alkanes. The medium acidity of the catalysts could also suppress carbon deposition as comparing to the strong ones. As shown in Figure 6, the carbon deposition over the spent 7 wt % Ni/SAPO-11 was 9%, while the value comparatively increased to 13% as the spent 7 wt % Ni/HZSM-5 was used. For all Ni based catalysts, the long chain alkanes with the carbon number of more than 16 (for example, heptadecane and octadecane) are possibly produced by coupling of long chain olefins dehydrated from the corresponding fatty alcohol and small cracking hydrocarbons,11,41 although the detailed formation mechanism needs to be further investigated.

4. CONCLUSIONS
Supported Ni catalysts on HY, HZSM-5, γ-Al2O3 and SAPO-11 were prepared by incipient wetness impregnation. γ-Al2O3 with large surface areas and pore sizes could highly disperse Ni particles via strong interactions. By contrast, the loaded Ni exclusively agglomerated into particles with sizes of several tens of nanometers over the external surface of SAPO-11, HZSM-5 and HY with the microchannels. The acidic sites and strength of the catalysts follows the order: 7 wt % Ni/γ-Al2O3 < 7 wt % Ni/SAPO-11 < 7 wt % Ni/γ-Al2O3 < 7 wt % Ni/HZSM-5 < 7 wt % Ni/HY. In HDO of methyl palmitate, Ni/SAPO-11 with weak and medium acidity showed the superior catalytic performance to the other catalysts due to the synergistic effect that the acidic sites of SAPO-11 promoted activation of methyl palmitate, followed by attacking of H atoms spilled over from metal Ni sites nearby, which obtained higher yield for the alkanes in diesel range. The maxim diesel-like alkane yield of 93% was observed over 7 wt % Ni/SAPO-11 under mild reaction condition, showing its promising catalytic application in this reaction.

Figure 6. TG curves of the used catalysts for (a) 7 wt % Ni/HZSM-5 and (b) 7 wt % Ni/SAPO-11.

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Notes
The authors declare that no competing interests exist.

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