Role of Support in Hydrotreatment of Jatropha Oil over Sulfided NiMo Catalysts

Shaofeng Gong, Akira Shinozaki, and Eika W. Qian*

The Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Nakacho 2-24-16, Koganei, Tokyo 184-8588, Japan

ABSTRACT: Hydrotreatment of jatropha oil over a series of sulfided NiMo/SiO$_2$–Al$_2$O$_3$ and NiMo/ZSM-5–Al$_2$O$_3$ catalysts in a fixed-bed reactor was carried out. Effect of support on various reactions occurring in hydrotreatment was investigated. For NiMo/SiO$_2$–Al$_2$O$_3$ series catalysts, the rates of decarboxylation and/or decarbonylation increased with increasing Si/(Si+Al) ratio, while the ratio of hydrodeoxygenation decreased with increasing Si/(Si+Al) ratio. For NiMo/ZSM-5–Al$_2$O$_3$ series catalysts, with increasing amounts of ZSM-5, the rate of decarboxylation and/or decarbonylation versus hydrodeoxygenation did not change. These results could be attributed to the total acidic sites of catalyst having a positive effect on the decarbonylation and/or decarboxylation pathways. NiMo/SiO$_2$–Al$_2$O$_3$ catalysts showed a much higher isomerization/cracking ratio than NiMo/ZSM-5–Al$_2$O$_3$ catalysts. It was suggested that isomerization reaction was favorable for weak and middle acidic sites but cracking reaction was favorable for strong acidic sites.

1. INTRODUCTION

Diminishing fossil resources and growing concerns about world environment necessitate the production of green fuels to substitute conventional fossil-derived ones by renewable resources. Recently, hydrotreatment of vegetable oils to produce green paraffinic fuels has attracted great attention and been considered to be one of the best routes for producing biofuels. Many studies have been conducted on the hydrotreatment of vegetable oils and some model compounds, such as palm oil, rapeseed oil, sunflower oil, jatropha oil, fatty acid, and ester. In these studies, traditional hydrodesulfurization catalysts such as sulfided NiMo/Al$_2$O$_3$, CoMo/Al$_2$O$_3$, and NiW/Al$_2$O$_3$ catalysts were mostly used, which showed that high hydrodeoxygenation activity and complete conversion of vegetable oil into hydrocarbons can be achieved.

It was well-known that there are three deoxygenation pathways in hydrotreatment of triglycerides, which were the main constituent of all vegetable oils. The first was hydrodeoxygenation, removing the oxygen by forming H$_2$O only and keeping the carbon atom number of the corresponding fatty acids. The second was decarbonylation, removing the oxygen by producing both CO and H$_2$O and leading to one carbon atom loss of corresponding fatty acid. The third was decarboxylation, removing the oxygen by formation of CO$_2$ and leading to one carbon atom loss of fatty acid. Şenol et al. proposed a reaction mechanism for hydrotreatment of methyl heptanoate in which heptanal was considered to be an intermediate leading selectivity to three deoxygenation pathways over sulfided NiMo and CoMo/Al$_2$O$_3$ catalysts. But they did not find any direct evidence and the deoxygenation mechanism remained to be investigated. Kublička et al. investigated the effect of active metals on deoxygenation pathway in hydrotreatment of rapeseed oil over sulfided Ni/Al$_2$O$_3$, Mo/Al$_2$O$_3$, and NiMo/Al$_2$O$_3$ catalysts and found that the deoxygenation pathway over Ni/Al$_2$O$_3$ catalyst was only compiled through decarboxylation and/or decarbonylation but the oxygen removal pathway over Mo/Al$_2$O$_3$ catalyst was executed primarily by hydrodeoxygenation. They also found that deoxygenation over NiMo/Al$_2$O$_3$ proceeded via both decarboxylation/decarbonylation and hydrodeoxygenation, and the ratio of Ni/Mo did not affect the deoxygenation pathway obviously. Hydrotreatment of jatropha oil over reduced PtPd/Al$_2$O$_3$ and sulfided NiMoP/Al$_2$O$_3$ catalysts was reported in our previous paper. It was found that the oxygen removal of jatropha oil over PtPd/Al$_2$O$_3$ catalyst proceeded primarily through decarboxylation and/or decarbonylation, but over NiMoP/Al$_2$O$_3$ catalysts, the oxygen removal proceeded primarily through hydrodeoxygenation. Although it was known that deoxygenation reactions were sensitive to the support of catalysts, the support effect in hydrotreatment of vegetable oils is ambiguous.

Because all the corresponding fatty acids in vegetable oil were straight-chain and their carbon numbers center at 16 and 18, the deoxygenated products of vegetable oil mainly consisted of $n$-alkanes from C$_{15}$ to C$_{18}$. These normal alkanes had a high cetane number (above 98) but their cold flow properties such as cloud point were so unfavorable that their application as diesel fuels was strictly limited. To resolve problems about the cold flow properties, isomerization of $n$-paraffin to branched isomers, which has been widely applied in petroleum industries such as dewaxing of lubricating oil, was regarded as an extremely feasible method. Hydrotreatment of vegetable oil over Pt/zeolites and PtRe/H-ZSM-5 catalysts in a batch reaction was studied. Results showed that high metal loading amount was needed to achieve complete deoxygenation and that the ratio of cracking/isomerization was very high on these catalysts. At the same time, it was found that H-ZSM-5 catalysts...
showed a higher ratio of iso-paraffin/\(n\)-paraffin and yield of hydrocarbon products than other zeolites such as HY, Beta, and MOR. Use of NiW/SiO\(_2\)−Al\(_2\)O\(_3\) catalysts to hydrotreat waste soya oil\(^{23}\) and use of NiMo/SiO\(_2\)−Al\(_2\)O\(_3\) catalysts to hydrotreat vegetable oils\(^{24}\) were also studied. Part of \(n\)-alkanes could be converted into iso-alkanes over these catalysts, but the selectivity of iso-alkanes was not enough to resolve the problems of poor cold flow properties, and the effects of the ratio of SiO\(_2\)/Al\(_2\)O\(_3\) and role of acidic sites in isomerization and cracking were not considered.

Although lots of studies about hydrotreatment of vegetable oils and model compounds were reported and interesting results were observed, the effect of support on deoxygenation pathway is yet ambiguous. Moreover, there are no papers to study the effect of support on isomerization and cracking reactions in hydrodreatment of vegetable oils. Thus, in the present study, a series sulfided NiMo/SiO\(_2\)−Al\(_2\)O\(_3\) and NiMo/ZSM-5−Al\(_2\)O\(_3\) catalysts were prepared and hydrodreatment of jatropha oil over these catalysts under suitable reaction conditions was conducted. Then the effect of support on deoxygenation, isomerization, and cracking reactions was further investigated.

2. EXPERIMENTAL SECTION

2.1. Feedstock and Catalysts. The feedstock used for catalyst activity evaluation was a kind of crude jatropha oil supplied by CREATAT-IPB and produced in Bogor, Indonesia.

Commercial supports \(\gamma\)-Al\(_2\)O\(_3\), two kinds of SiO\(_2\)−Al\(_2\)O\(_3\) (SA-1 and SA-2), and SiO\(_3\) were supplied by Nippon Ketjen. Three other supports, which were denoted Z-S, Z-10, and Z-30 (5, 10, and 30 wt % addition of ZSM-5 in the supports), were prepared according to the following procedure: First, ZSM-5 (supplied by Catalysis Society of Japan, JRC-Z5-70H, SiO\(_2\)/Al\(_2\)O\(_3\) = 70, specific surface area 322 m\(^2\)/g), \(\gamma\)-Al\(_2\)O\(_3\) and binder (boehmite, 20 wt %) were milled into powder and mixed. The mixture and a small amount of deionized water were put into a Teflon beaker, followed by intensive stirring to make a mudlike solid. Then the mudlike solid was pressed and shaped into small cylinders with an experimental scale model. Finally, the small cylinders were dried at room temperature for 12 h and calcined in a Muffle furnace at 550 °C for 3 h. All the supports were crushed and sieved to a 20–80 mesh particle size fraction before metal loading.

All catalysts were prepared following a conventional successive impregnation procedure as reported.\(^{25}\) The respective support was loaded with Mo and Ni with aqueous solutions of \((NH_4)_6Mo_7O_{24}\) and \(Ni(NO_3)_2\) to achieve a loading amount of 20 wt % MoO\(_3\) and 3.5 wt % NiO in which Mo was introduced first. After impregnation, the samples were dried at 105 °C for 2 h and then calcined at 450 °C for 10 h under air flow.

2.2. Catalyst Characterization. Elemental analysis was conducted on an X-ray fluorescence instrument (EDX-800, Shimadzu). The samples were pressed into disks before analysis. Specific surface areas and pore sizes were determined from the nitrogen adsorption and desorption isotherms and recorded at \(-196 °C\) by use of a Belsorp-mini II device (Bel Japan). Before the measurements, the samples were degassed under vacuum at 400 °C for 1 h. The specific surface areas and pore volumes were calculated by the BET (Brunauer−Emmett−Teller) method. Then, the average pore sizes were calculated from desorption isotherm branches by the BJH (Barrett−Joyner−Halenda) method. NH\(_3\)-TPD (ammonia temperature-programmed desorption) experiments were carried out on a chemisorption physisorption analyzer (ChemBET Pulsar TPR/TPD, Quantachrome) according to the following procedure. First, about 200 mg of sample was put into the sample cell and pretreated at 500 °C under helium flow for 3 h at 15 mL/min. After cooling to 100 °C, ammonia adsorption was carried out for 40 min under ammonia flow at 15 mL/min. Physically adsorbed ammonia was removed with blowing helium at 100 °C for 2 h. Finally, NH\(_3\)-TPD of the samples was carried out by increasing the cell temperature linearly from 100 to 650 °C with a heating rate of 10 °C/min and a helium flow rate of 15 mL/min.

2.3. Activity Test of Catalysts. Details of the apparatus were also described in an earlier report.\(^{26}\) In short, the reactions were conducted with a fixed-bed flow microreactor (ø 8 mm i.d.). About 3 mL of catalyst was loaded and sandwiched by quartz sands in the reactor. The feedstock was injected by a high-pressure pump into the hydrogen stream. The reaction was conducted at 330–370 °C, 3 MPa of total pressure, LSHV (liquid hourly space velocity) = 2 h\(^{-1}\), and \(H_2/\text{feed}\) ratio of 600 (v/v). Before reaction, all the catalysts were sulfided in situ at 400 °C and atmospheric pressure by a mixture of 5 vol % \(H_2S\) and 95 vol % \(H_2\) at a rate of 50 mL/min for 3 h. Catalytic activity was measured after stabilization of the catalyst (all the time on-stream was about 10 h). In all experiments, no significant deactivation of the various catalysts was observed during 10 h of reaction. Reaction products were separated into gas and liquid first and then the liquid products were separated into water and oil phases.

Two gas chromatographs (GC-17A and GC-14B; Shimadzu), equipped with an FID (flame ionization detector) and a commercially available column (DB-1, 0.25 mm ×60 m), were used to analyze the hydrocarbons in the gaseous and liquid products, and a gas chromatograph/mass spectrometer (GCMS-QP5050A; Shimadzu) equipped with the same capillary column (DB-1, 0.25 mm × 60 m) was used to identify the components of the reaction hydrocarbon products. Another gas chromatograph with a TCD (thermal conductivity detector) and a commercial column (Unibeads C, 3 mm ×3 m) was used to determine other components, such as CO and CO\(_2\) in gaseous products. Additionally, a CP-TAP CB for triglycerides column (0.25 mm ×25 m) was used to analyze the heavy products such as mono-, di-, and triglycerides.

3. RESULTS AND DISCUSSION

3.1. Feedstock Analysis. The composition of the feedstock to be hydrotreated has a direct effect on the consumption of hydrogen and the distribution of the hydrocarbon products. Some physical and chemical properties of the crude jatropha oil were determined, and the results are presented in Table 1. Density and dynamic viscosity were determined by use of a hydrometer (JIS-II) and a dynamic viscometer (SV-10A, Vibro). The acid value was determined by titration with a standard solution of potassium hydroxide in ethanol according to ASTM-D974. Fatty acid compositions of the feedstock were determined by gas chromatography after transesterification and esterification with methanol. The fatty acid composition of jatropha oil and their contents are also presented in Table 1. From the analysis results, jatropha oil had a high dynamic viscosity of 25.32 mPa⋅s at 25 °C, generated by the triglycerides, and a high acid value of 7.86 mg of KOH/g, caused by the free fatty acid. Fatty acids mainly found in jatropha oil were palmitoleic, linoleic, oleic, palmitic, and stearic
Table 1. Properties and Fatty Acid Composition of Jatropha Oil

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>0.91</td>
</tr>
<tr>
<td>Dynamic viscosity, mPa·s/25 °C</td>
<td>25.32</td>
</tr>
<tr>
<td>Acid value, mg of KOH/g</td>
<td>7.86</td>
</tr>
<tr>
<td>Fatty acid composition, C mass %</td>
<td></td>
</tr>
<tr>
<td>Palmitoleic acid (C₁₆:1)</td>
<td>0.93</td>
</tr>
<tr>
<td>Palmitic acid (C₁₆:0)</td>
<td>13.62</td>
</tr>
<tr>
<td>Linoleic acid (C₁₈:2)</td>
<td>36.21</td>
</tr>
<tr>
<td>Oleic acid (C₁₈:1)</td>
<td>43.39</td>
</tr>
<tr>
<td>Stearic acid (C₁₈:0)</td>
<td>5.85</td>
</tr>
</tbody>
</table>

Table 2. Chemical Compositions and Textural Properties of Several NiMo Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SiO₂ (wt %)</th>
<th>NiO</th>
<th>MoO₃ (wt %)</th>
<th>S₄₉₈⁰⁺(m²/g)</th>
<th>Vₑₙ₈⁰⁺(cm³/g)</th>
<th>d₄₅⁻⁺(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/Al₂O₃</td>
<td>0.2</td>
<td>3.2</td>
<td>19.3</td>
<td>219</td>
<td>0.615</td>
<td>11.2</td>
</tr>
<tr>
<td>NiMo/Z-5</td>
<td>3.4</td>
<td>3.4</td>
<td>19.6</td>
<td>187</td>
<td>0.503</td>
<td>10.8</td>
</tr>
<tr>
<td>NiMo/Z-10</td>
<td>6.8</td>
<td>3.3</td>
<td>18.8</td>
<td>184</td>
<td>0.463</td>
<td>10.0</td>
</tr>
<tr>
<td>NiMo/Z-30</td>
<td>20.3</td>
<td>3.4</td>
<td>17.5</td>
<td>187</td>
<td>0.377</td>
<td>8.1</td>
</tr>
<tr>
<td>NiMo/SA-1</td>
<td>4.2</td>
<td>3.5</td>
<td>18.1</td>
<td>219</td>
<td>0.651</td>
<td>11.9</td>
</tr>
<tr>
<td>NiMo/SA-2</td>
<td>9.1</td>
<td>3.4</td>
<td>17.6</td>
<td>215</td>
<td>0.687</td>
<td>12.8</td>
</tr>
<tr>
<td>NiMo/SiO₂</td>
<td>79.6</td>
<td>3.2</td>
<td>16.9</td>
<td>225</td>
<td>0.852</td>
<td>15.2</td>
</tr>
</tbody>
</table>


acids, each of which had a straight-chain structure. The fatty acids with carbon numbers of 16 and 18 had carbon molar percentages of 14.55% and 85.45%, respectively. The saturated and unsaturated fatty acid contents were respectively 19.47% and 80.53%.

3.2. Characterization of Catalysts. All calcined catalysts were prepared according to the same procedure, and we tried to achieve the same loading amount. Although different supports were employed, final metal oxide loadings determined by X-ray fluorescence (XRF) in all catalysts (as presented in Table 2) were approximately the same. For all catalysts, cobalt oxide loading varied within the range 3.2−3.5 wt %, whereas loadings of molybdenum oxide ranged from 16.9 to 19.6 wt %. The SiO₂ contents were as follows: NiMo/Al₂O₃, 0.2 wt %; NiMo/SA-1, 4.2 wt %; NiMo/SA-2, 9.1 wt %; NiMo/SiO₂, 79.6 wt %; NiMo/Z-5, 3.4 wt %; NiMo/Z-10, 6.8 wt %; and NiMo/Z-30, 20.3 wt %.

The textural properties derived from adsorption−desorption isotherms of nitrogen on the calcined catalysts are also shown in Table 2. NiMo/Al₂O₃, NiMo/SA-1, NiMo/SA-2 and NiMo/SiO₂ catalysts had similar specific surface areas (220 ± 5 m²/g). But due to the addition of binder, NiMo/Z-5, NiMo/Z-10, and NiMo/Z-30 catalysts had lower specific surface areas (184−187 m²/g) than the catalysts mentioned above. It was also found that the pore volume and average pore size of the catalysts increased with the addition of SiO₂ but decreased with the addition of ZSM-5.

The surface acidity properties of all oxidized NiMo catalysts were investigated by means of NH₃-TPD. The NH₃-TPD profiles of all catalysts are illustrated in Figure 1. As shown in Figure 1, each catalyst showed a different distribution of acidic sites. NiMo/Al₂O₃ and NiMo/SiO₂ catalysts showed a broad peak, while the other catalysts showed two partially overlapping peaks. To compare the acidity distribution among the catalysts, the NH₃-TPD profiles were separated into two or three peaks by curve-fitting with Gaussian functions. These peaks were divided into three categories, 216−231, 278−336, and 433−448 °C, which represented weak, medium, and strong acidity, respectively. According to the published study,27,28 three kinds of adsorbed ammonia species could be assigned to NH₃ weakly adsorbed on the Lewis acid site, NH₃⁺ on the Bronsted acid site, and strong adsorbed on and/or interacted with the dislodged Al, respectively. The amounts of desorbed ammonia for each type of acidic site were calculated and are listed in Table 3. Each catalyst showed a different quantity for each type of acidic site. The quantity of weak and medium acidic sites decreased in the same order: NiMo/SA-2 > NiMo/SA-1 > NiMo/SiO₂ > NiMo/Al₂O₃ > NiMo/Z-5 > NiMo/Z-10 > NiMo/Z-30. However, the quantity of strong acidic sites decreased in the order NiMo/Z-30 > NiMo/Z-10 > NiMo/Z-5 >> other catalysts. Namely, the addition of ZSM-5 brought an increase of strong acidic sites; however, the addition of SiO₂ brought an increase of weak and medium acidic sites.

3.3. Hydrotreatment of Jatropha Oil over NiMo/SiO₂−Al₂O₃ Catalysts. In the present study, the hydrocarbon products under all hydrotreatment conditions were determined by two GCs and divided into four ranges: gaseous hydrocarbon products C₁−₄, cracked liquid hydrocarbon products C₅−₁₄ deoxygenated hydrocarbon products C₁₅−₃₀, and heavy hydrocarbon products C₃₁. The hydrocarbon products represented a simple mixture containing mainly n-paraffins (mainly n-C₅−₃₀). Beside n-paraffins, the liquid hydrocarbon product also contained small amounts of iso-paraffins and trace amounts of cycloalkanes and aromatics. Some oxygenates, for example, fatty acid, fatty alcohol, and monoglycerides, were considered...
to be the intermediates in hydrodeoxygenation of jatropha oil, were found in some cases. However, the contents of these oxygenates were very low and they were donated into C18+. A CHNS/O elemental analyzer was also used to determine the elemental composition of liquid hydrocarbon products. It was found that the oxygen content was lower than 0.05% for all samples. Because the deoxygenation was higher than 99.5% in all cases, it will not be described in the following discussion. We also detected some special products including CO, CO2, and H2O derived from the deoxygenation reactions and H2.

The total hydrocarbon yield of C1−18 products over four catalysts was summarized and it was high, up to 93% ± 2%. Because the carbon mole percents in CO, CO2, and C18+ are still not included, we can safely conclude that almost all triglycerides in the jatropha oil were converted into hydrocarbons. It was found that the Si/(Si+Al) ratio of NiMo/SiO2−Al2O3 catalysts had only a slight impact on the yields of different fraction. The yield of C1−4, C5−14, and C18+ products increased as the Si/(Si+Al) ratio increased from 0.002 to 0.11, and then slightly decreased as the Si/(Si+Al) ratio increased further to 0.99. However, the yield of C15−18 products showed an opposite tendency as the Si/(Si+Al) ratio increased. In comparison with the NH3-TPD results (Table 3), the decrease of C1−14 products and increase of C1−4 and C15−18 products could be attributed to the increase in acidity of the catalyst, which resulted in increasing cracking activity of the catalyst.

To get a better understanding of reaction mechanism before the subsequent discussion, it is necessary to describe the pathway of triglyceride deoxygenation. According to previous works9,13,16,17 it is considered that three deoxygenation pathways exist in triglyceride hydrotreatment, as shown in eqs 1−3. One mole of Cn (where n denotes the carbon number) fatty acid group in the triglyceride generates 1 mol of CO + 1 mol of H2O (decarboxylation, eq 1), 1 mol of CO + 1 mol of H2O (decarbonylation, eq 2), or 2 mol of H2O (hydrodeoxygenation, eq 3). The oxygen is removed by generating 1 mol of CO2 (decarboxylation, eq 1), 1 mol of CO + 1 mol of H2O (decarbonylation, eq 2), or 2 mol of H2O (hydrodeoxygenation, eq 3). It should be noted that H2 consumption increases in the order decarboxylation (1 mol of H2 required) < decarbonylation (2 mol of H2 required) < hydrodeoxygenation (4 mol of H2 required). From an economic perspective, decarboxylation is considered to be the best reaction pathway.

\[
\text{R-CH}_2\text{-COOA + H}_2 \rightarrow \text{AH + R-CH}_3 + \text{CO}_2 \quad (1)
\]

\[
\text{R-CH}_2\text{-COOA + 2H}_2 \rightarrow \text{AH + R-CH}_3 + \text{CO} + \text{H}_2\text{O} \quad (2)
\]

\[
\text{R-CH}_2\text{-COOA + 4H}_2 \rightarrow \text{AH + R-CH}_2\text{-CH}_3 + \text{2H}_2\text{O} \quad (3)
\]

where

\[
\begin{align*}
\text{(A):} & \quad \text{CH}_2\text{-COOR}^1, \quad \text{CH}_3, \quad \text{CH}_2\text{-COOR}^1 \text{ and } \text{CH}_4 \\
\text{R-CH}_2\text{-COOA:} & \quad \text{CH}_2\text{-COOR}^2, \quad \text{CH}_3, \quad \text{R-CH}_2\text{-COOR}^2 \text{ and } \text{CH}_4
\end{align*}
\]

In addition to the deoxygenation reactions, some other reactions such as water gas shift (eqs 4) and methanation (eqs 5 and 6) may occur among CO, CO2, and H2O derived from the deoxygenation reactions and H2.

Table 3. Acidity Properties of Several NiMo Catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>weak T (°C)</th>
<th>acidity (μmol/g)</th>
<th>medium T (°C)</th>
<th>acidity (μmol/g)</th>
<th>strong T (°C)</th>
<th>acidity (μmol/g)</th>
<th>total acidity (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/Al2O3</td>
<td>231</td>
<td>18.0</td>
<td>314</td>
<td>38.2</td>
<td></td>
<td></td>
<td>56.2</td>
</tr>
<tr>
<td>NiMo/Sa-1</td>
<td>221</td>
<td>29.5</td>
<td>330</td>
<td>67.0</td>
<td></td>
<td></td>
<td>96.5</td>
</tr>
<tr>
<td>NiMo/Sa-2</td>
<td>223</td>
<td>33.9</td>
<td>336</td>
<td>77.0</td>
<td></td>
<td></td>
<td>110.9</td>
</tr>
<tr>
<td>NiMo/SiO2</td>
<td>216</td>
<td>23.5</td>
<td>278</td>
<td>43.9</td>
<td></td>
<td></td>
<td>67.4</td>
</tr>
<tr>
<td>NiMo/Z-5</td>
<td>217</td>
<td>13.3</td>
<td>291</td>
<td>37.3</td>
<td>433</td>
<td>10.5</td>
<td>61.1</td>
</tr>
<tr>
<td>NiMo/Z-10</td>
<td>221</td>
<td>12.7</td>
<td>288</td>
<td>37.0</td>
<td>441</td>
<td>16.1</td>
<td>65.8</td>
</tr>
<tr>
<td>NiMo/Z-30</td>
<td>221</td>
<td>12.0</td>
<td>291</td>
<td>36.8</td>
<td>448</td>
<td>24.8</td>
<td>73.6</td>
</tr>
</tbody>
</table>

Figure 2. Hydrocarbon product yields in hydrotreatment of jatropha oil over several NiMo/SiO2−Al2O3 catalysts (T = 350 °C, LHSV = 2 h−1, P = 3 MPa, H2/oil = 600 mL/mL). Figure 2 shows the yields of different fractions of hydrocarbon products. The yield of C1−4 products ranged from 6.1% to 6.4%. Most of this fraction was propane (about 5.7%), which was mainly generated from the hydrogenation of glycerol group in jatropha oil.13 The yield of C5−14 products, which was produced by the cracking reactions, ranged from 0.9% to 3.0%. The C15−18 fraction was the major product with carbon yields from 82.4% to 88.2%. This fraction was generated from the deoxygenation of free fatty acid groups in jatropha oil. The yield of C18+ products varied from 2.4% to 5.0%. Some identified results (as determined by GC-MS) showed that these fractions mainly contained heavy alkanes (C19−24) and trace amount of oxygenates (such as fatty acid, fatty alcohol, and monoglycerides). Triglycerides and diglycerides were not determined in this fraction.
As described above, because CO, CO₂, and H₂O were the products formed in three deoxygenation pathways, it was interesting to study the deoxygenation pathway by studying the formation rates of CO, CO₂, and H₂O. It was found that the formation rate of methane was much lower than those of carbon oxides and water (see Figures 3b, 5b, and 7). In addition, part of methane was also formed via cracking reaction. This indicated that the methanation reactions (eqs 5 and 6) were much slower than deoxygenation reactions and could be ignored in comparison with deoxygenation reactions (eqs 1–3). To further investigate the deoxygenation pathway, the methanation reactions are ignored in the following discussion.

Because both eqs 2 and 4 generate 1 mol of H₂O at the same time they generate 1 mol of CO, while eq 3 generates 2 mol of H₂O but does not generate CO, (H₂O−CO) could be regarded as the generated H₂O of eq 3. And furthermore, (H₂O−CO)/2 could be regarded as the reaction rate of hydrodeoxygenation (eq 3). However, due to the presence of water gas shift reaction, the formation rates of CO₂ and CO could not be regarded as the rates of decarboxylation and decarbonylation, respectively. Therefore, the formation rates of CO₂ and CO were added together to used to study the total rate of decarboxylation and/or decarbonylation. The formation rates of total carbon oxides and (H₂O−CO)/2 were calculated and are showed in Figure 3b. With increasing Si/(Si+Al) ratio, the formation rate of carbon oxides increased but the formation rate of (H₂O−CO)/2 decreased. These results indicated that the rates of decarbonylation and hydrodeoxygenation increased with increasing Si/(Si+Al) ratio, while the ratio of hydrodeoxygenation decreased with increasing Si/(Si+Al) ratio.

The normal alkanes C₁₅−₁₈ produced from deoxygenation of jatropha oil can be ideal additives for diesel fuel due to their high cetane numbers. However, large amounts of normal alkanes in diesel fuel may also cause bad cold flow properties, and partial isomerization of the normal alkanes is desired. The yields of isomerized products and cracked products are shown in Figure 3c. All alkanes except normal alkanes in C₁₅−₁₈ and all alkanes from C₆ to C₁₄ except propane, were separately regarded as the isomerized products and cracked products. From Figure 3c, the yield of cracked products was at a low level (below 3.84%) over all NiMo/SiO₂−Al₂O₃ catalysts. The yield of isomerized products increased up to 22.91% as the Si/(Si+Al) ratio increased from 0.002 to 0.11 catalyst and then decreased as the Si/(Si+Al) ratio increased to 0.99.

In this case, the yields of isomerized products were too low to improve the cold flow properties (the cloud point of liquid hydrocarbon products over NiMo/SA-2 catalyst was 9 °C). Thus, further work should focus on how to develop more efficient catalysts to obtain higher branched isomers during the hydrotreatment of vegetable oil.

3.4. Hydrotreatment of Jatropha Oil over NiMo/ZSM-5−Al₂O₃ Catalysts. To investigate the effect of another solid acid support, ZSM-5, for hydrotreatment of vegetable oil, hydrotreatment of jatropha oil over various NiMo/ZSM-5−Al₂O₃ catalysts (NiMo/Z-5, NiMo/Z-10, and NiMo/Z-30) was carried out under conditions of T = 350 °C, LHSV = 2 h⁻¹, P = 3 MPa, H₂/oil = 600 mL/mL. Figure 4 shows the yields of different fractions. The yields of C₁−₄ and C₅−₁₄ fractions increased with increasing addition of ZSM-5, while the yields of C₁₅−₁₈ fractions decreased with increasing addition of ZSM-5. The yields of C₁−₄, C₅−₁₄, and C₁₅−₁₈ fractions were respectively 16.62%, 41.24%, and 40.34% over NiMo/Z-30 catalyst. It was concluded that the triglycerides in jatropha oil products. This was because jatropha oil comprised of fatty acid group with C₁₈ and C₁₆ mainly, which formed C₁₇ and C₁₅ alkanes by decarbonylation and/or decarboxylation pathways, and formed C₁₈ and C₁₆ alkanes by hydrodeoxygenation pathway (as described above). With increasing the Si/(Si+Al) ratio, the yields of C₁₅ and C₁₇ alkanes increased, but the yields of C₁₆ and C₁₈ decreased. It meant that the deoxygenation pathway was affected by the support.
were mostly converted into alkanes over all NiMo/ZSM-5−Al2O3 catalysts by looking at the low yield of C18+ and high total hydrocarbon yield of C1−C18 products (96% ± 2%). Figure 5a shows the product yields of C15, C16, C17, and C18 alkanes. With increasing added amounts of ZSM-5, the yields of C15, C16, C17, and C18 alkanes decreased significantly. This was because ZSM-5, with high cracking activity, converted the deoxygenation products, C15−C18 alkanes, into light hydrocarbons, C1−C14 alkanes, as shown in Figure 4. It was interesting that the ratio of C15+C17/C16+C18 almost did not change with changing the addition of ZSM-5, which meant that decarbonylation plus decarboxylation versus hydrodeoxygenation did not change with addition of ZSM-5 (if the differences in cracking rate between C15, C16, C17, and C18 are ignored). From Figure 5b, it was observed that the formation rate of methane was much lower than those of carbon oxides and water even though NiMo/ZSM-5−Al2O3 catalysts had high cracking activity and could generate a lot of methane. This result indicated that the methanation reaction was still much slower than deoxygenation reactions on NiMo/ZSM-5−Al2O3 catalysts. The formation rates of carbon oxides and (H2O−CO)/2 almost did not change with increasing added amounts of ZSM-5, which indicated that the rate of decarboxylation and/or decarbonylation versus hydrodeoxygenation did not change with increased addition of ZSM-5. This result was consistent with the similar ratio of C15+C17/C16+C18. Figure 5c shows the yields of isomerized products and cracked products. The yields of isomerized products remained at a low level (below 4.50%) over all NiMo/ZSM-5−Al2O3 catalysts. But the yields of cracked products increased sharply as the addition of ZSM-5 increased. We attempted to reduce the cracking and increase isomerization by decreasing reaction temperature over NiMo/Z-30 catalyst. At 330 °C, the yield of cracked products was still high. At 310 °C, a solid white wax product was formed, which was a mixture of saturated triglycerides, free fatty acid, and other oxygenates (as determined by GC-MS). It meant that cracking could not be simply reduced by lowering the reaction temperature over NiMo/Z-30 catalyst, because lower reaction temperature also caused the loss of deoxygenation activity.

Both hydrocracking and hydroisomerization reactions were widely recognized to process essentially through carbenium ion mechanism, in which acid properties of a support played a key role. The mechanism of isomerization and cracking of a linear paraffin started with a first step of formation of a carbenium ion. The carbenium ion was likely first isomerized by skeletal rearrangement on an acidic site. Then the branched carbenium ion could continue to be cracked into a smaller alkylcarbenium ion and alkane by β-scission on the acidic site or be desorbed to generate an isomer product. Cracking was also considered to be a consecutive reaction, which was favored for multibranched alkanes. It was believed that the isomerization/cracking ratio depended on facts such as strength of the acid sites, type of active metal, porous structure of support, reaction conditions, etc., in which the density and strength of acidic sites were the most important, and an adequate balance between these parameters was critical for catalyst activity. In the present study, it could be found that the yields of isomerized products increased with middle acidic site and the yields of cracked products increased with strong acidic site (as shown in Table 3 and Figures 3 and 5). NiMo/SiO2−Al2O3
catalysts that had more medium acidic sites but no strong acidic sites showed much higher isomerization/cracking ratios than NiMo/Al2O3−ZSM-5 catalysts that had more strong acidic sites but few medium acidic sites. Consequently, it could be concluded that the isomerization reaction was favorable for middle acidic sites but the cracking reaction was favorable for strong acidic sites for hydrotreatment of vegetable oil under our experimental conditions.

3.5. Effects of Support on Catalytic Performance. Catalytic activities of NiMo/Al2O3, NiMo/SA-2, and NiMo/Z-10 catalysts were investigated under the conditions \( T = 330−370 ^\circ C \), LHSV = 2 h\(^{-1}\), \( P = 3 \) MPa, and \( H_2/oil = 600 \) mL/mL. Figure 6 portrays the yields of isomerized products and cracked products over NiMo/Al2O3, NiMo/SA-2, and NiMo/Z-10 catalysts (LHSV = 2 h\(^{-1}\), \( P = 3 \) MPa, \( H_2/oil = 600 \)).

Another probable reason for low isomerization activity of NiMo/Al2O3−ZSM-5 catalysts was the diffusion limit. It was reported that the critical diameter of the triglyceride molecule was around 2 nm\(^{30,31}\) whereas ZSM-5 only had medium pores of about 0.56 nm \( \times \) 0.53 nm\(^{32}\) which is much smaller than triglyceride molecule. Therefore, the molecules of triglycerides obviously could not diffuse through the ordered micropores of ZSM-5, and efficient contact between triglyceride molecule and active site was mainly possible only on the external surface of ZSM-5. The triglyceride molecule must be converted to hydrocarbons by deoxygenation first and then react with the active site on the inert surface of ZSM-5. But NiMo/SiO2−Al2O3 catalysts had average pore diameter of 11.9−15.2 nm, which was much bigger than triglyceride molecules. This meant that the diffusion of triglyceride molecules on the NiMo/SiO2−Al2O3 catalysts was much easier than on the NiMo/Al2O3−ZSM-5 catalysts.

To investigate the effect of reaction temperature and support types on the deoxygenation pathway, Figure 7 shows the formation rates of carbon oxides (panel a) and \((H_2O−CO)/2\) (panel b) over NiMo/Al2O3, NiMo/SA-2, and NiMo/Z-10 catalysts (LHSV = 2 h\(^{-1}\), \( P = 3 \) MPa, \( H_2/oil = 600 \)).

Figure 6. Effect of reaction temperature on yields of (a) isomerized products and (b) cracked products over NiMo/Al2O3, NiMo/SA-2, and NiMo/Z-10 catalysts (LHSV = 2 h\(^{-1}\), \( P = 3 \) MPa, \( H_2/oil = 600 \)).

Figure 7. Effect of reaction temperature on formation rates of (a) carbon oxides and (b) \((H_2O−CO)/2\) over NiMo/Al2O3, NiMo/SA-2, and NiMo/Z-10 catalysts (LHSV = 2 h\(^{-1}\), \( P = 3 \) MPa, \( H_2/oil = 600 \)).
rates of decarboxylation and/or decarbonylation but lower rate of hydrodeoxygenation than NiMo/Al2O3 and NiMo/ZSM-5–Al2O3, which was consistent with change in quantity of total acidic sites: NiMo/Al2O3 had much more acidic sites than NiMo/Al2O3 and NiMo/Z-10. Thus the total acidic sites of catalyst could have a positive effect on the decarboxylation and/or decarbonylation pathway.

4. CONCLUSIONS
A series of sulfided NiMo/SiO2−Al2O3 and NiMo/ZSM-5−Al2O3 catalysts were prepared and used in hydrotreatment of jatropha oil in a fixed-bed flow reactor. A remarkable support effect on the deoxygenation pathways was observed. For NiMo/SiO2−Al2O3 catalysts, the rates of decarboxylation and/or decarbonylation increased with increasing Si/(Si+Al) ratio, while the ratio of hydrodeoxygenation decreased with increasing Si/(Si+Al) ratio. For NiMo/ZSM-5−Al2O3 catalysts, the rate of decarboxylation and/or decarbonylation versus hydrodeoxygenation did not change with increasing addition of acidic sites.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: whqian@cc.tuat.ac.jp.

Notes
The authors declare no competing financial interest.

■ REFERENCES