Hydroprocessing of Jatropha oil over NiMoCe/Al₂O₃ catalyst

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ABSTRACT

The non-sulfided NiMoCe/Al₂O₃ catalyst was developed to produce green diesel from the hydroprocessing of Jatropha oil. The NiMoCe/Al₂O₃ catalysts were prepared by impregnation and characterized by N₂-BET, SEM, XRD and TPD-H₂ads techniques. The straight chain alkanes ranging from C₁₅ to C₁₈ were the main components in product oil. The maximum yield of C₁₅-C₁₈ alkanes of 80%, selectivity of 90% and conversion of 89% were obtained at 370°C, 3.5 MPa and 0.9 h⁻¹. Influence of reaction temperature (280–400°C) and reaction time (10–163 h) on the composition of product oil were discussed. The experimental results demonstrated that a suitable amount of metal Ce doping on the NiMo/Al₂O₃ catalyst presented stable catalytic performance and enhanced Jatropha oil conversion as well as C₁₅-C₁₈ fraction selectivity.

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1. Introduction

There is a worldwide trend of searching for renewable energy sources for production of transportation fuels due to the diminishing fossil fuel reserves and environmental challenges associated with the greenhouse effect. The biofuels derived from plant oils are environmentally friendly because they are free of nitrogen and sulfur compounds [1]. Hydroprocessing of vegetable oil leads to the production of hydrocarbons in the boiling range of diesel, and therefore it is commonly called green diesel or renewable diesel [2]. The hydroprocessed products are straight chain alkanes consisting of 15–20 carbons, which after isomerization are very similar to present fossil diesel [3,4].

Hydroprocessing has been developed to produce straight chain alkanes from fatty acid triglycerides of animal fat, tall oil, and other vegetable oils. Metal sulfide catalysts have been widely used for vegetable oil hydroprocessing [4–6], and other types of catalysts such as noble metal catalysts have been also reported [7]. The transition metal catalysts required the addition of sulfur-containing compounds (such as H₂S) for keeping the catalysts in the active form [8]. It should be paid attention that under long-term conditions the sulfur could leach out from the catalysts and the quality of green diesel might be affected if the products had sulfur residuals [9]. On the other hand, the toxicity and corrosivity of H₂S could bring great harm to the environment, human health and instruments. Although noble metal catalysts were non-sulfided, they were much expensive and not suitable for the large-scale process.

Commonly used transition metal catalysts were the sulfided NiMo, CoMo and NiW based catalysts containing P, B, Cu et al. [10] However, much less emphasis has been placed on catalysts containing rare earth metal. Lanthanide or actinide metals combined with some metals (namely Ni, Co, Cu or Fe) were described as new type of supported catalysts precursors, which can be more active [11]. It has been reported that cerium promote activity of nickel/alumina catalysts in CO hydrogenation [12]. Metallic catalysts promoted with cerium...
are interesting due to cerium properties that can improve their thermal stability, metallic dispersion, catalytic activity and decrease the carbon deposition [13, 14]. Thus, the main aim of this work was to develop the non-sulfided NiMo/Al2O3 catalyst containing Cerium (Ce) for the green diesel production. Hydroprocessing of vegetable oil such as soybean, sunflower and rapeseed has been reported [15–17]. Considering the problem of biofuels competing with food sources, non-edible plant oil (Jatropha oil) was used as the feedstock to produce green diesel for the transportation fuel. In this work, we investigated hydroprocessing of Jatropha oil over NiMoCe/Al2O3 catalyst.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst NiMo (5wt.%Ni, 15wt.%Mo) was prepared by wet coimpregnation of aqueous solutions of (NH4)6Mo7O24 and Ni(NO3)2 on the support Al2O3 grain. Then the NiMo/Al2O3 catalysts were dried overnight at 105 °C and calcined at 400 °C for 4 h. The NiMo/Al2O3 catalysts (where x indicated Ce content from 1 to 25wt.%) were prepared by impregnation of NiMo/Al2O3 catalyst with a solution containing Ce(NO3)3. Impregnated samples were dried overnight at 105 °C and calcined at 400 °C for 4 h.

N2 adsorption-desorption using a V-Sorb 2800 TP Surface Area and Pore Distribution Analyzer instrument of catalyst evacuated at 300 °C for 4 h was used to determine specific surface areas and pore size distributions. Specific surface area was obtained by the common Brunauer, Emmett and Teller (BET) procedure. The external surface area and the area of the micropores were determined by the t-plot method. Pore size distribution (pore diameter and pore volume) was calculated by Barret-Joyner-Halenda (BJH) method from the adsorption branch of the isotherms. All textural parameters were normalized also per gram of support.

Electron microscopy images of samples were taken with CamScan Apollo300 scanning electron microscope (SEM) equipped with X-ray energy-dispersive (EDX) microanalyzer (OXFORD INCA). X-ray diffraction (XRD) was used to determine the structural properties of the catalysts. These measurements were performed by Empyrean XRD analyzer (Cu-Kα) and PIXcel1D detector from PANalytical Company. These samples were measured in the 2θ range from 10° to 80° (scan speed of 0.02° per second).

Temperature programmed desorption (TPD) experiments were performed using a TP-5080 Multi-functional Automatic Adsorption Instrument from Tianjin Xianquan Company. 100 mg of catalyst samples were pretreated under N2 atmosphere at 400 °C for 20 min prior to reduction. Adsorption of hydrogen was carried out under a mixed stream of H2 (30 ml/min) and N2 (30 ml/min) in two stages: firstly at constant temperature of 400 °C for 1 h and then at gradually decreasing temperature from 400 °C to 20 °C. After the reduction, the examined sample was flushed with a N2 stream (30 ml/min, 20 °C, 0.25 h) to remove weakly adsorbed hydrogen and strongly adsorbed hydrogen was examined by TPD method. The TPD-H2ads examination was carried out in an N2 stream of 30 ml/min at linearly increasing temperature of 10 °C/min from 20 °C to 1000 °C. The amount of desorption H2 was monitored on-line by a GC equipped with a TCD.

2.2. Catalytic activity measurements

Jatropha oil was purchased from Jiangsu Donghu Bioenergy Co., Ltd. The distribution of fatty acids were as follows: myristic acid 0.1%, palmitoleic acid 1.2%, palmitic acid 14.8%, linolenic acid 0.9%, linoleic acid 36.2%, oleic acid 38.3%, stearic acid 7.3%, arachidic acid 0.5%.

The experiments were performed in a fixed-bed reactor equipped with electrically heating system. A detailed description of the apparatus was given elsewhere [18]. The non-sulfided catalyst (10 g) was loaded into the stainless steel tubular reactor (1.2 cm ID and 56 cm in length) and activated in situ prior to the experiments using H2 at 400 °C and 3.5 MPa for 3 h, while the sulfided NiMo catalysts were activated in situ prior to the experiments with 5 vol.% dimethyl disulfide (DMDS) in isoctane at 350 °C and 3.5 MPa for 4 h. The reaction conditions for catalytic hydroprocessing experiment were as follows: temperature 280–400 °C, pressure 3.5 MPa, LHSV 0.9 h−1, and H2 to feed ratio of 1000 mL H2 gas/mL liquid feed.

The liquid products were withdrawn after stabilization of reaction conditions (10 h) in two-hour intervals and analyzed by off-line gas chromatography (GC) after separation of the water phase. The gaseous products and water were not further analyzed. The liquid products were analyzed using a GC-900C equipped with AT. SE-30 column (L = 30 m, d = 0.32 mm, tf = 0.5 μm) and detected using a flame ionization detector (FID). Helium was used as the carrier gas. The following temperature program was used: initial temperature 160 °C for 5 min, heating 10 °C/min to 260 °C, with dwelling time of 10 min at 260 °C. The individual products were identified using GC standards. The conversion of Jatropha oil was calculated as:

\[
C = 100\% - C_{\text{TG}}
\]

where \(C_{\text{TG}}\) is the concentrations of triglycerides (%) in the product oil determined by GC analysis. The selectivity of C15-C18 alkanes was calculated as:

\[
S = \frac{Y}{C} \times 100\%
\]

where \(Y\) is yield of the C15-C18 alkane (%) determined by GC analysis and \(C\) is the conversion of Jatropha oil (%) calculated by Eq. (1).

Infrared method using for the analysis of product oil were carried out on a Fourier transform infrared spectrometer (FTIR-650) from a thin liquid film over a KBr window. The FTIR spectra correspond to the sum of 32 scans at a 1.5 cm⁻¹ spectral resolution.

3. Results and discussion

3.1. Catalyst characterization

Basic characteristics of the support and catalysts used in testing are shown in Table 1. Al2O3 supports have considerably...
high surface area (311.4 m²/g) and large pore diameter (5.8 nm), which would readily allow the diffusion of bulky triglyceride molecules. Impregnation of Ni, Mo and Ce on Al₂O₃ support leads to a decrease in the specific surface area. The decrease in the specific surface area is higher after the impregnation of NiMoCe(25) on Al₂O₃ support (46%) in comparison with the impregnation of NiMoCe(1) and NiMoCe(5) on Al₂O₃ support (15% and 18%). The decreases in the specific surface area and total pore volume suggest that the addition of Ni, Mo and Ce blocked some pores in the Al₂O₃ support [19].

Fig. 1 shows that Ni, Mo and Ce species distributed on the alumina surface as it was evidenced from SEM-EDX images of NiMoCe(5)/Al₂O₃ catalyst. The light dots represent Ni, Mo and Ce, while alumina surface is depicted in dark color. It can be seen that Ni, Mo and Ce species are evenly distributed on the alumina surface and no aggregates can be observed.

The XRD profiles of Al₂O₃ support, NiMo/Al₂O₃ and NiMoCe(5)/Al₂O₃ catalysts are shown in Fig. 2. The peaks of NiMo/Al₂O₃ and NiMoCe/Al₂O₃ catalysts exhibit lower crystallinity, compared to the parent Al₂O₃ support, indicated by an obvious decrease in the intensity of diffraction peaks at 2θ = 14.5°, 28.4°, 38.3°, 49.2°. Compared with NiMo/Al₂O₃ catalyst, most peaks of NiMoCe/Al₂O₃ catalyst are weaker, indicating that the additives rare earth metal could increase the dispersion of NiMoO, leading to the formation of more active center and adsorbing more hydrogen. This result is in accordance with the works of Jianqiang Zhu et al. [20]. Impregnated Ce is believed to exist as CeO₂ on Al₂O₃ after calcination [21]. Diffraction peaks appear at 2θ = 28.6°, 33.1°, 47.5°, and 56.4° corresponding to CeO₂ for 5wt.% (i.e., NiMoCe5) are stronger than NiMo/Al₂O₃ catalyst [22]. No additional diffraction peaks assignable to CeAlO₃ or Ce₂O₃ are seen in the X-ray spectra [23].

The TPD-H₂ads spectra obtained for NiMo/Al₂O₃ catalyst, NiMoCe(5)/Al₂O₃ catalyst and NiMoCe(25)/Al₂O₃ catalyst (Fig. 3) represent one broad profiles at 700–800 °C. It can be seen that the desorption temperature of the catalysts shifted to higher temperature with increasing Ce content. According to the literature [20,24], it can be inferred that nickel species strongly interact with alumina and the interaction between

| Table 1 – Physicochemical properties of Al₂O₃ support and NiMoCe/Al₂O₃ catalysts. |
|----------------|----------------|----------------|----------------|
|                | Al₂O₃          | NiMoCe(1)      | NiMoCe(5)      | NiMoCe(25)    |
| Specific surface areas, m²/g | 311.4          | 263.2          | 256.8          | 167.4         |
| Micropore area, m²/g | –              | 29.2           | 18.1           | 10.1          |
| External surface area, m²/g | 234.0          | 238.7          | 157.3          |
| Total pore volume, cm³/g | 0.4            | 0.4            | 0.4            | 0.2           |
| Average pore diameter, nm | 5.8            | 6.2            | 6.0            | 5.9           |

Fig. 1 – SEM-EDX images of NiMoCe(5)/Al₂O₃ catalyst calcined at 400 °C.
NiO and Al₂O₃ is remarkably improved after the addition of Ce, leading to the high desorption temperatures. Furthermore, the spectra show that Ce additives can markedly enhance H₂ uptake as compared with NiMo/Al₂O₃ catalyst, and the peak height of NiMoCe(5)/Al₂O₃ and NiMoCe(25)/Al₂O₃ catalysts (670 ppm and 780 ppm respectively) are both more than that of NiMo/Al₂O₃ catalyst (630 ppm).

3.2. Hydroprocessing of Jatropha oil

3.2.1. Effect of reaction temperature on the composition of product oil

In general, temperature is the main parameter for hydroprocessing of vegetable oil [25]. Thus, the effect of reaction temperature on the composition of product in the hydroprocessing of Jatropha oil over NiMoCe(5)/Al₂O₃ catalyst is investigated and the result is shown in Fig. 4. It can be seen that the maximum yield 80% of the C₁₅-C₁₈ fraction is observed at 370 °C. The yield of C₁₅-C₁₈ hydrocarbons greatly increases from 280 °C to 370 °C. There is no significant effect on the yield of C₁₅-C₁₈ at the reaction temperature from 370 °C to 400 °C. The heavy fraction (>C₁₈) gradually decreases, which mainly contains long chain esters formed by esterification of alcohol and free fatty acid [26]. The light fraction (<C₁₅) yield increases with temperature, as higher temperatures favor cracking and the consequent production of smaller molecule hydrocarbons.

The GC charts of liquid products obtained by hydroprocessing of Jatropha oil over NiMoCe(5)/Al₂O₃ catalyst at the reaction temperatures range from 280 °C to 400 °C are presented in Fig. 5. It can be clearly seen that the main
components in product oil are the straight chain alkanes ranging from C15 to C18. Heptadecane and octadecane are the two most abundant liquid alkanes, which are produced from the fatty acids of the triglycerides. Fig. 5 shows the concentration of smaller molecule increases with increasing reaction temperature, while that of large molecules is decreased. This means that the cracking of Jatropha oil is accelerated at higher temperature.

Jatropha oil is hydrotreated at reaction temperatures ranging from 280 °C to 400 °C over the NiMoCe(S)/Al2O3, NiMo/Al2O3 and sulfided NiMo/Al2O3 catalysts. The results for conversions of Jatropha oil are shown in Fig. 6. It can be seen that the conversions increase with increasing reaction temperature and at the highest temperature (400 °C), conversion approaches 97% over NiMoCe/Al2O3 and sulfided NiMo/Al2O3 catalyst while 84% over NiMo/Al2O3 catalyst. Thus, the NiMoCe/Al2O3 catalyst shows a higher conversion as compared with NiMo/Al2O3 catalyst, which is mainly attributed to the content of Ce. At the temperature 400 °C, the conversions over NiMoCe/Al2O3 and sulfided NiMo/Al2O3 catalyst are almost the same (97%), while the conversion over NiMoCe/Al2O3 catalyst is lower than sulfided NiMo/Al2O3 catalyst at the temperature from 280 °C to 370 °C. Thus, in order to improve the catalytic activity and increase the conversion of Jatropha oil, we are searching for other rare earth metals and supports.

In order to compare the hydroprocessing activity of NiMoCe(1–25)/Al2O3 catalyst with sulfided and non-sulfided NiMo/Al2O3, hydroprocessing reactions of Jatropha oil are carried out. As shown in Table 2, all NiMoCe/Al2O3 catalysts show high hydrodeoxygenation activity at 370 °C. The yields of C15–C18 are 68–80% and the conversions into alkanes are 76–89%. Although the conversion of sulfided NiMo/Al2O3 is highest, the C15–C18 fraction selectivity of that is lower than NiMoCe(1–25)/Al2O3. Therefore, the hydroprocessing activity of non-sulfided NiMoCe/Al2O3 catalyst is almost the same as that of sulfided NiMo/Al2O3 catalyst. Table 2 also shows that NiMo/Al2O3 catalyst gives higher other composition, such as long chain esters formed by esterification of alcohol and free fatty acid [26], because hydrogenation activity of NiMo/Al2O3 is lower than sulfided NiMo/Al2O3 and NiMoCe/Al2O3.

According to the products distribution, the reaction mechanism for the hydroprocessing over NiMoCe/Al2O3 catalyst is presumed to have two routes. One is hydrodeoxygenation (HDO) yielding hydrocarbons with even carbon number (mainly C16 and C18), the other is hydrodecarboxylation (HDC) yielding hydrocarbons with odd carbon number (mainly C15 and C17). This is in agreement with the literature reported on deoxygenation [3,27,28]. Table 2 shows the (C15 + C17)/(C16 + C18) ratio increases with increasing Ce-content (NiMoCe1/Al2O3 < NiMoCe5/Al2O3 < NiMoCe25/Al2O3). It can be deduced that HDC enhances with increasing Ce-content and HDC route is much more favored than HDO route.

The results show rare earth metal (Ce) functions as an activity promoter of NiMo catalysts in hydrogenation activity. This is because rare earth oxides are well known as weak Lewis basic compounds and have the ability to donate electrons. It has demonstrated that the lanthanide species on the surface of the NiMo/Al2O3 catalyst might donate electrons to the Ni oxide species, resulting in an increase in electron density on these metal oxides, and might form a complex structure with Ni [21]. That high hydrogenation activity of NiMoCe/Al2O3 catalyst is most probably attributed to such unique structure, which cooperates with the hydrogenation metal site Ni to act as a potential hydrogen supply. We can speculate that a suitable amount of metal Ce doping on the

Table 2 – Hydroprocessing of Jatropha oil on different catalysts (370 °C, 3.5 MPa, 0.9 h−1).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NiMo</th>
<th>Sulfided NiMo</th>
<th>NiMoCe(1)</th>
<th>NiMoCe(5)</th>
<th>NiMoCe(25)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;C15</td>
<td>7.7</td>
<td>5.7</td>
<td>8.3</td>
<td>7.0</td>
<td>9.6</td>
</tr>
<tr>
<td>C15</td>
<td>5.5</td>
<td>4.2</td>
<td>8.5</td>
<td>9.5</td>
<td>10.4</td>
</tr>
<tr>
<td>C16</td>
<td>5.6</td>
<td>9.1</td>
<td>6.8</td>
<td>7.9</td>
<td>9.2</td>
</tr>
<tr>
<td>C17</td>
<td>20.9</td>
<td>28.5</td>
<td>27.3</td>
<td>37.2</td>
<td>35.4</td>
</tr>
<tr>
<td>C18</td>
<td>21.7</td>
<td>35.5</td>
<td>25.4</td>
<td>25.4</td>
<td>19.7</td>
</tr>
<tr>
<td>Other hydrocarbons and esters</td>
<td>37.9</td>
<td>17.0</td>
<td>22.8</td>
<td>12.9</td>
<td>14.8</td>
</tr>
<tr>
<td>(C15 + C17)/(C16 + C18)</td>
<td>1.0</td>
<td>0.7</td>
<td>1.1</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Conversion</td>
<td>67.5</td>
<td>95.4</td>
<td>76.1</td>
<td>88.9</td>
<td>81.7</td>
</tr>
<tr>
<td>C15-C18 selectivity</td>
<td>79.5</td>
<td>81.0</td>
<td>89.3</td>
<td>90.0</td>
<td>91.3</td>
</tr>
</tbody>
</table>

a Not specified hydrocarbons and esters of heavy fraction.
NiMo/Al₂O₃ catalyst can increase the amount of hydrogen adsorbed on the catalyst. This assumption is supported by TPD-H₂ ads spectra (Fig. 3) where NiMoCe/Al₂O₃ catalyst markedly enhances H₂ uptake as compared with NiMo/Al₂O₃ catalyst. The enhanced reducibility and adsorbed hydrogen of NiMoCe/Al₂O₃ catalyst by acid support help to increase the hydrocracking activity of such catalyst.

### 3.2.2. Influence of reaction time-on-stream for NiMoCe/Al₂O₃ catalyst

Fig. 7 shows the yields of C₁₅-C₁₈ alkanes as a function of reaction time using NiMoCe(5)/Al₂O₃ catalyst. It can be seen that the alkanes yield is nearly constant with time from 10 h to 163 h of reaction. However, there is gradual decrease in C₁₇ alkane yield along with gradual increase in C₁₈ alkane yield. Such a variation is also visible in case of C₁₆ and C₁₅.

Fig. 8 shows the conversion of Jatropha oil and ratio of (C₁₅ + C₁₇)/(C₁₆ + C₁₈) in product oil after reaction time of 163 h. The conversion of Jatropha oil is always more than 75% during the entire course of reaction. There is no significant variation in the conversion with time from 10 h to 163 h of reaction. This indicates that the NiMoCe(5)/Al₂O₃ catalyst performance is stable for extended reaction time.

The ratio of C₁₅ and C₁₇ to C₁₆ and C₁₈ can serve as an indicator for assessing the reaction course of HDC and HDO. As shown in Fig. 8, the (C₁₅ + C₁₇)/(C₁₆ + C₁₈) ratio slowly decreases from 1.1 to 0.5 with reaction time. That means with increasing reaction time there is a gradual shift in reaction mechanism from HDC towards HDO. Such a variation may be due to that the cracking ability of the catalyst slowly recedes with reaction time which leading to the increase of C₁₈ and C₁₆ yields. While the decrease of C₁₇ and C₁₅ yields are attribute to HDO increase along with HDC decrease.

### 3.2.3. Infrared analyses

IR spectra of C₁₅-C₁₈ alkanes standard, product oil and Jatropha oil are showed in Fig. 9. The spectrum of Jatropha oil (g) shows absorbance bands characteristic of triglyceride at 1150–1350 cm⁻¹ and 1747 cm⁻¹ attributed to C=O and C=O stretching vibration, respectively. The main differences between Jatropha oil and standard of alkanes (a) are the peaks mentioned above. In addition, they both exhibit the bands associated with saturated C–H stretching vibration (CH, CH₂ and CH₃) at 2700–3000 cm⁻¹.

Analyzing only the spectra of product oil, it is observed that characteristic band of fatty acid (1735 cm⁻¹) has lower intensity in product oil obtained from Jatropha oil over NiMoCe(1–25)/Al₂O₃ catalyst (c–e) than that over NiMo/Al₂O₃ catalyst (f). This fact evidences the deoxygenating activity of NiMoCe/Al₂O₃ catalyst is better than that of NiMo/Al₂O₃ catalyst. It can be seen that NiMoCe(5)/Al₂O₃ catalyst shows the best deoxygenating activity among the different Ce-content. Moreover, the product oil over sulfided NiMo/Al₂O₃ catalyst (b) shows almost the same intensity at 1735 cm⁻¹ and deoxygenating activity as NiMoCe(5)/Al₂O₃ catalyst (d). In short, Jatropha oil is converted to alkanes, fatty acids and some low oxygenates [29,30].

It can be concluded that metal...
Ce doping on the NiMo/Al₂O₃ catalyst can increase HDO/HDC activity and the product oil primarily are saturated alkanes.

4. Conclusion

In conclusion, green diesel (renewable liquid alkanes) can be produced from hydrotreatment of Jatropha oil over NiMoCe/Al₂O₃ catalyst. The hydrocarbon yield of C15-C18 was 80%, the selectivity was 90% and the conversion was 89% at 370°C, 3.5 MPa and 0.9 h⁻¹ using NiMoCe/Al₂O₃ catalyst (Ce 5wt.%). GC charts showed the concentration of smaller molecule species of rare earth metal catalyst for the hydroprocessing of Jatropha oil can eliminate the sulfurization step and avoid the cation of rare earth metal catalyst. The hydrocarbon yield of C15-C18 was 80%, the sulfur content was 0.2% and the conversion was 89% at 370°C, 3.5 MPa and 0.9 h⁻¹ using NiMoCe/Al₂O₃ catalyst (Ce 5wt.%). GC charts showed the concentration of smaller molecule species of rare earth metal catalyst for the hydroprocessing of Jatropha oil can eliminate the sulfurization step and avoid the cation of rare earth metal catalyst.

References