Short communication

A cleaner process for hydrocracking of jatropha oil into green diesel

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ABSTRACT

To achieve cleaner processing, Ni-HPW/Al₂O₃ was synthesized as a new green catalyst for producing biodiesel, and jatropha oil was transformed into hydrocarbons (primarily n-C₁₅ to n-C₁₈ alkanes) using the new catalyst. A 99.85% jatropha oil conversion rate and 85.52% selectivity of the n-C₁₅ to n-C₁₈ fractions were obtained at a temperature of 360 °C, a pressure of 3.3 MPa, a H₂/ oil volume ratio of 600 (N m³)/m³, and a liquid hourly space velocity of 1.0 h⁻¹. It was also observed that higher reaction temperatures clearly favored oxygen removal from the hydrocracking products. During hydrocracking, the new catalyst was efficient and avoided H₂S pollution; it therefore has potential for use in the biodiesel industry.

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1. Introduction

Fossil fuels are not a sustainable resource, and consequently the development of liquid biofuels is becoming increasingly important [1]. Fatty acid methyl esters (FAMEs), a type of biofuel [2–5], can be produced by the transesterification of triglycerides with methanol using a heterogeneous catalyst such as Amberlyst or sulfated zirconia [6,7]. However, FAMEs suffer from some drawbacks, such as the formation of sludge after long storage, sensitivity to hydrolysis, and autoxidation [8,9].

Hydrocracking is being explored as an alternative approach for biofuel production, because it can transform vegetable oils into hydrocarbons (mainly C₁₅–C₁₈) using bifunctional heterogeneous catalysts such as NiMo/Al₂O₃ or NiW/Al₂O₃ [10,11]. The hydrocracking method for producing FAMEs [10,11], the hydrocracking method for biofuels needs a higher temperature (300–400 °C), and more energy, to crack vegetable oils into hydrocarbons, but the hydrocracking products have increased oxidation stability and higher cetane numbers.

The conventional catalysts used in hydrocracking are alumina-supported sulfided forms of NiMo or CoMo [12,13]. However, the use of these catalysts requires the addition of sulfur-containing compounds, for example H₂S or dimethyl disulfide, to maintain the catalysts in an active form [14]. The addition of sulfiding agents causes sulfur residues in the products, H₂S emissions, and corrosion problems.

The growing awareness of the unacceptability of these conventional sulfided catalysts has given a major impetus to the search for cleaner catalysts. In addition to their environmentally favorable characteristics, heteropolyacids have attracted much attention as efficient catalysts because of their unique composition, which includes heteropolyanions and counter-cations. As a result, heteropolyacids have been used both as acid and oxidation catalysts in a wide variety of reactions [15–17]. For these reasons, phosphotungstic acid (HPW) has been included as part of a new catalyst design for hydrocracking of triglycerides. The non-sulfided catalyst Ni-HPW/Al₂O₃ was synthesized, and the effects of temperature (as the dominant parameter) on the effectiveness of hydroprocessing with the new catalyst were investigated.

2. Materials and methods

2.1. Chemicals

Phosphotungstic acid and nickel nitrate were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Al₂O₃ (φ = 2–3 mm) was obtained from Beijing Donghuan Union Chemical Co., Ltd, China. 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%, and arachic acid 0.5%. The C₁₈ TAGs accounted for 82% proportion of the Jatropha oil. The iodine value of the Jatropha oil was 105.2 mg I₁/100 g. Standards of n-C₁₁ to n-C₁₈ were purchased from Sigma–Aldrich Co., LLC.
2.2. Preparation of catalyst

The Ni-HPW/Al2O3 catalyst was prepared by a two-step impregnation method. First, Al2O3 samples were impregnated with a solution containing a given amount of HPW in deionized water. The solvent was completely removed at 60 °C in a rotary evaporator and the HPW/Al2O3 solids were calcined at 400 °C for 3 h in dry air. Second, the HPW/Al2O3 solids were impregnated with a solution containing nickel nitrate in deionized water. The solvent was evaporated at 90 °C in a rotary evaporator until a dry material was obtained. The catalyst was then calcined at 400 °C for 2 h.

2.3. Catalyst characterization

Scanning electron microscopy (SEM) images of the catalysts were obtained using an SC 3400 scanning electron microscope (Camscan Company). Quantitative compositional analysis was carried out with an INCA Energy energy-dispersive X-ray analysis (EDAX) system attached to the electron microscope. Determination of the chemical composition was based on the average analytical data of individual particles.

X-ray diffraction (XRD) was used to determine the catalyst structure. Measurements were performed using an Empyrean XRD analyzer (Cu Kα) and a PIIXcel® detector (PANalytical Company). Samples were measured in the 2θ range from 10° to 80° at a scan speed of 0.02°/s.

N2 adsorption isotherms were measured using a NOVA-1000 instrument (Quantachrome Instruments, Boynton Beach, FL, USA). Before the measurements were made, samples were degassed in a vacuum at 300 °C for 4 h. The surface areas and pore size distributions of the samples were investigated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda analyses, respectively. The total pore volume was calculated from the volume of N2 adsorbed at a relative pressure, p/p0, of 0.97.

The acidities of the catalysts were determined by temperature-programmed desorption of ammonia using a TPDRO 1100 analyzer (Thermo Fischer Scientific, Waltham, MA, USA). All samples were pretreated in N2 (25 mL/min) at 325 °C for 2 h. The desorption step was performed from 100 °C to 700 °C at a heating rate of 10 °C/min.

Fourier-transform infrared (FT-IR) spectra were recorded in the wavenumber range 500–4000 cm⁻¹ using 32 scans and a resolution of 4 cm⁻¹ with a FT-IR spectrometer (GANDDONG 650).

Thermogravimetric analysis (TGA) was performed using a NETZSCH STA449F3 analyzer to determine the amount of carbon deposited on the used catalysts. Samples were first heated from 30 °C to 550 °C at a heating rate of 30 °C/min in N2, using a flow rate of 100 mL/min. The temperature was maintained at 550 °C for 15 min, and then the samples were heated linearly at 30 °C/min to 900 °C in a flow of 100 mL/min of O2. The weight losses of the samples were processed using a microcomputer.

2.4. Hydrocracking experiments

The hydrocracking of jatropha oil was performed in a fixed-bed reactor (JF-2, Tianjing Golden Eagle Technology Co., Ltd, China). The pilot plant (see Fig. 1) for continuous hydrocracking can be divided into the following sections: (1) feed system, (2) pre-heating section, (3) tubular reactor, (4) condensation section, (5) storage section, and (6) instrumentation and control section. The reaction temperature was computer controlled and the system pressure was maintained using a back-pressure regulator. Jatropha-seed oil was delivered from a feed tank into the reactor using a high-pressure pump. The hydrogen input rate was controlled using a separate mass-flow meter.

Prepared catalyst (10 g) was loaded in the fixed-bed reactor (inner diameter 12 mm). The catalyst was activated in a hydrogen stream at 400 °C for 3 h.

Fig. 1. Schematic diagram of test apparatus (FC-01, 02, gas flow meters; TC01-08, pre-heaters; TI-09, thermocouple; and PT-01, pressure meter).
Table 1
Physical properties of alumina support and catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Average pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>300.39</td>
<td>4.64</td>
<td>0.34</td>
</tr>
<tr>
<td>Catalyst</td>
<td>136.27</td>
<td>4.33</td>
<td>0.14</td>
</tr>
</tbody>
</table>

2.5. Product analysis

A gas chromatograph (GC) equipped with a flame-ionization detector (GC900C, Tianpu Co., Ltd, Shanghai, China) was used. The capillary column (ATSE-30, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences) dimensions were 0.32 mm i.d. × 30 m with a film thickness of 0.5 μm. n-Alkane standards were used to estimate the relative percentages and distributions of the products with respect to their carbon numbers.

FT-IR spectroscopy was used to determine the structures of the products. FT-IR spectra were recorded in the wavenumber range 500–4000 cm⁻¹, using 32 scans and a resolution of 4 cm⁻¹, with a FT-IR spectrometer (GANGDONG 650).

The iodine values of the samples were determined in accordance with the ASTM D5554-95 standard method.

3. Results and discussion

3.1. Catalyst characterization

The surface areas, pore volumes, and average pore sizes of the alumina support and the Ni-HPW/Al₂O₃ catalyst are listed in Table 1. The average pore size of the catalyst was located in the typical mesopore range. It can be seen that the impregnation of Ni and HPW species into the alumina support decreased the specific surface area, pore volume, and average pore size in comparison to those of the support. It was suspected that Ni and HPW species plugged the support pores, and therefore the specific surface area and pore volume decreased.

SEM photographs were obtained to observe the surface morphology of the Ni-HPW/Al₂O₃ catalyst. As can be seen from Fig. 2, the catalyst had a rough surface, and cracks could be found on the catalyst. EDAX measurements were made to determine the chemical composition of the catalyst, and quantitative analysis of different elements showed that the catalyst contained 5.54 wt% Ni, 28.49 wt% W, and 0.38 wt% P. EDAX mapping (Fig. 2) indicated that most of the Ni, W, and P in the newly synthesized catalyst was homogeneously distributed in the alumina support.

The FT-IR spectrum of the catalyst is shown in Fig. 3. The peaks at 1080, 985, 890, and 811 cm⁻¹ correspond to ν(P–O), ν(W=O), ν(W–O–W) edge, and ν(W–O–W) corner, respectively [18]. This indicates that the Keggin structure of HPW was preserved in the catalyst.

The XRD profiles of the Al₂O₃ support and the Ni-HPW/Al₂O₃ catalyst are shown in Fig. 4. The peaks of the Ni-HPW/Al₂O₃ catalyst show a lower crystallinity than that of the parent Al₂O₃ support, indicated by an obvious decrease in the intensities of the diffraction peaks at 2θ = 14.5°, 28.4°, 38.3°, and 49.2°. The Ni oxide phase (37.0°, 43.1°, and 62.6°) was not observed; this may be because the Ni species impregnated in the support are highly dispersed, forming an amorphous surface compound. The characteristics peaks for HPW (10.5°, 25.5°, 34°) are observed.
[19], indicating that the HPW was maintained on the support after calcination at a temperature of 400 °C.

To investigate the Ni oxidation state, the Ni-HPW/Al2O3 was examined using X-ray photoelectron spectroscopy (XPS). As shown in Fig. 5, the binding energy of Ni in the region near 853 eV and 861 eV could be associated with Ni2+ ions [20]. The results indicate that the Ni species on the catalyst are present as Ni2+

3.2. Catalytic activity

For comparison, the catalytic activities of conventional catalysts, i.e. sulfided NiW/Al2O3 and NiW/Al2O3, were compared with Ni-HPW/Al2O3 under the same conditions (temperature 300–360 °C, liquid hourly space velocity 1.0 h⁻¹, pressure 3.3 MPa, and H2/oil volume ratio 600 (N m³)/m³). It can be seen in Fig. 6 that the activity of the Ni-HPW/Al2O3 catalyst is similar to that of sulfided NiW/Al2O3, whereas the activity of NiW/Al2O3 is clearly lower than those of the sulfided NiW/Al2O3 and Ni-HPW/Al2O3 catalysts. The acidities of the three catalysts were in the following order: sulfided NiW/Al2O3 > Ni-HPW/Al2O3 > NiW/Al2O3 (see Table 2). This trend is consistent with the activities of the three catalysts. Typically, hydropretreatment catalysts consist of metal sites and acidic sites. The metal sites (Ni, Co, Mo, and W) catalyze hydrogenation/dehydrogenation, and the acidic sites catalyze the cracking function [21]. The sulfided NiW/Al2O3 has a higher activity than the non-sulfided NiW/Al2O3, partly because the sulfur species increase the catalyst acidity, which promotes the cracking function of the catalyst [22]. The Ni-HPW/Al2O3 catalyst prepared from the corresponding heteropolyacid showed better performance in hydrocracking of oil than did its counterpart NiW/Al2O3 prepared from the traditionally used W ammonium salts. The reasons for the high catalytic activity of the Ni-HPW/Al2O3 catalyst seem to be related to its high acidity and its Keggin-type structure. The Ni-HPW/Al2O3 catalyst not only possesses similar activity to that of the sulfided NiW/Al2O3, but also avoids serious the H2S pollution caused by conventional catalysts such as sulfided NiW/Al2O3. The catalyst can therefore be considered as a candidate for use in producing biofuels.

3.3. Effect of reaction temperature on composition of product oil

The oil conversion rates and the selectivities for the different reaction products were calculated from chromatographic data (reaction conditions: liquid hourly space velocity 1.0 h⁻¹, pressure 3.3 MPa, and H2/oil volume ratio 600 (N m³)/m³).

The gas chromatograms of the hydrocracking products obtained at various reaction temperatures are shown in Fig. 7. The primary products were n-C15H32, n-C16H34, n-C17H36, and n-C18H38. As shown in Fig. 8, the product composition was strongly influenced by the reaction temperature. The total n-C15 to n-C18
content of the product markedly increased with increasing temperature because of higher conversion of triglycerides to alkanes; the highest total n-C\textsubscript{15} to n-C\textsubscript{18} yield of 85.52 wt\% was obtained at 360 °C. Above 360 °C, the n-C\textsubscript{15} to n-C\textsubscript{18} content decreased, whereas the lighter hydrocarbon fraction content gradually increased. It is plausible that higher reaction temperatures also resulted in increased cracking of n-C\textsubscript{15} to n-C\textsubscript{18} products to shorter-chain hydrocarbons.

3.4. Selectivity in reaction pathways over Ni-HPW/Al\textsubscript{2}O\textsubscript{3} catalyst

The pathways for conversion of jatropha oil to biodiesel are shown in Fig. 9. Hydrodeoxygenation (HDO) leads to removal of oxygen in the form of water, and the resulting hydrocarbon has the same number of carbon atoms as the corresponding fatty acid bound in the original triglyceride. In contrast to HDO, hydrodecarboxylation or hydrodecarbonylation (HDC) leads to elimination of carboxylic groups in the form of carbon dioxide or carbon monoxide, and the resulting hydrocarbon has one carbon less than the corresponding fatty acid bound in the original triglyceride [23].

n-C\textsubscript{17}H\textsubscript{36} is the main product of the HDC pathways, whereas n-C\textsubscript{18}H\textsubscript{38} is the main product of the HDO pathway. The relative ratios of the HDC and HDO pathways are therefore revealed by the ratio of the yields of n-C\textsubscript{17}H\textsubscript{36} to n-C\textsubscript{18}H\textsubscript{38} products.

At a reaction temperature of 320 °C, the n-C\textsubscript{17} peak is lower than that of n-C\textsubscript{18} (see Fig. 7), whereas at 380 °C, the n-C\textsubscript{17} peak is higher than that of n-C\textsubscript{18}. The ratio of C\textsubscript{17} to C\textsubscript{18} increases from 0.68 to 1.61 as the reaction temperature increases from 300 °C to 380 °C, which means that higher temperatures favored HDC over HDO on the Ni-HPW/Al\textsubscript{2}O\textsubscript{3} catalyst. This result is in agreement with previous studies with sulfided catalysts [17]. A consequence of this finding is that the cetane number of the resulting biofuel can be controlled because the relative n-C\textsubscript{17} or n-C\textsubscript{18} content can be determined by adjusting the reaction temperature.

![Fig. 9. Pathways for conversion of jatropha oil to biodiesel.](image-url)
3.5. Oxygen removal

Fig. 10 shows the FT-IR spectra of the products obtained at various reaction temperatures (reaction conditions: liquid hourly space velocity 1.0 h⁻¹, pressure 3.3 MPa, and H₂/oil volume ratio 600 (N m⁻³)/m³). After the hydrocracking reaction, the jatropha oil peak at 3010 cm⁻¹, corresponding to the double-bond stretching vibration, is lost, with the iodine value decreasing form 105.2 to 0 mg I₂/100 g, indicating that the double bonds were saturated in this process.

Oxygen is undesirable in the final products. The peaks at 2927 and 2854 cm⁻¹ are assigned to asymmetric CH₂ stretching and symmetric CH₂ stretching, respectively. The peaks at 1745 and 1710 cm⁻¹ are both assigned to the carbonyl functional group. The peaks at 1350–1500 cm⁻¹ correspond to angular deformation of CH₂ and CH₃. The peak at 1159 cm⁻¹ is assigned to saturated acyl groups, and the peak at 721 cm⁻¹ is assigned to asymmetric angular deformation in the CH₂ plane.

Fig. 10 also shows that an increase in the reaction temperature results in a decrease in the oxygen-related absorption peaks at 1745, 1710, and 1159 cm⁻¹. This indicates that a higher reaction temperature clearly favors oxygen removal from the products.

3.6. Stability of Ni-HPW/Al₂O₃ catalyst

The stability of the catalytic properties of the Ni-HPW/Al₂O₃ catalyst was investigated (at temperature 360 °C, liquid hourly space velocity 1.0 h⁻¹, pressure 3.3 MPa, and H₂/oil volume ratio 600 (N m⁻³)/m³) during 240 h on stream. Fig. 11 shows the yields of C₁₅–C₁₈ alkanes as a function of reaction time using the Ni-HPW/Al₂O₃ catalyst. It can be seen that the selectivity of the catalyst for C₁₅–C₁₈ alkanes was nearly constant with time. At the beginning of the experiment, the conversion was 68.5%; after 20 h on stream, the conversion remained steady at 99.8%, up 240 h, when the conversion decreased to 76.3%. There were no significant variations in the selectivity and conversion for long time-periods. This indicated that the Ni-HPW/Al₂O₃ catalyst performance was stable for extended reaction times.

After a catalytic run of 240 h, the spent Ni-HPW/Al₂O₃ catalyst was regenerated by keeping it inside the reactor in a H₂ flow at 400 °C for 3 h, and then heating it in an air flow at 445 °C to remove organic compounds. In order to determine coke formation, which would deactivate the catalyst, the changes in the amounts of carbon deposited on the catalysts were determined by TGA, based on ISO 6964-1986. Fig. 12 and Table 3 show that after regeneration, the carbon residue on the catalyst decreased from 4.38% to 1.59%, and the activity of the catalyst increased by 24% compared with the spent catalyst; this may be the result of a decrease in coke deposition on the catalyst. The Ni and W contents of the catalyst were constant, indicating that the metals in the catalyst did not leach out in the hydrocracking process. The results show that the catalyst was reusable, and after regeneration it still performed well in the next hydrocracking cycle.

![Fig. 10. FT-IR spectra of products at different reaction temperatures with the Ni-HPW/Al₂O₃ catalyst. Reaction conditions: pressure 3.3 MPa, liquid hourly space velocity 1.0 h⁻¹, and H₂/oil volume ratio 600 (N m⁻³)/m³.](image)

![Fig. 11. Conversions and yields of C₁₅–C₁₈ alkanes as a function of reaction time using Ni-HPW/Al₂O₃ catalyst. Reaction conditions: pressure 3.3 MPa, liquid hourly space velocity 1.0 h⁻¹, and H₂/oil volume ratio 600 (N m⁻³)/m³.](image)

![Fig. 12. TGA profiles of (a) spent Ni-HPW/Al₂O₃ and (b) regenerated Ni-HPW/Al₂O₃.](image)

**Table 3**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weight of coke (wt%)</th>
<th>Ni content (wt%)</th>
<th>W content (wt%)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>-</td>
<td>5.54</td>
<td>28.49</td>
<td>99.8</td>
</tr>
<tr>
<td>Spent catalyst</td>
<td>4.38*</td>
<td>5.23</td>
<td>28.23</td>
<td>76.3</td>
</tr>
<tr>
<td>Regenerated catalyst</td>
<td>1.59</td>
<td>5.39</td>
<td>28.31</td>
<td>93.5</td>
</tr>
</tbody>
</table>

*On-stream time of 240 h at pressure 3.3 MPa, liquid hourly space velocity 1.0 h⁻¹, and H₂/oil volume ratio 600 (N m⁻³)/m³.
4. Conclusions

In the current study, a heteropolyacid (phosphotungstic acid) was used in the synthesis of a hydrocracking catalyst. A 99.8% conversion of jatropha oil and over 85.52% selectivity of the diesel fraction were obtained at a temperature of 360 °C, a pressure of 3.3 MPa, a liquid hourly space velocity of 1.0 h⁻¹, and a H₂/oil volume ratio of 600 (N m⁻³)/m³. It was observed that higher temperatures favored HDC in hydrocracking and also favored oxygen removal from the products. This green catalyst not only showed high activity, but also did not leave sulfur residues in the product, thus reducing sulfur emissions. This new Ni-HPW/Al₂O₃ catalyst has great potential as an alternative to sulfided catalysts for producing biodiesel.

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