Hydrocracking of DDGS Corn Oil over Transition Metal Carbides Supported on Al-SBA-15: Effect of Fractional Sum of Metal Electronegativities

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Abstract

Nickel-based carbide catalysts combined with four different metals (Mo, Nb, W, and Zr) and supported on Al-SBA-15 were investigated for the hydrocracking of distillers dried grains with solubles (DDGS) corn oil to produce biofuels under mild reaction conditions. The effects of the fractional sums of the electronegativities of the transition metals on the catalyst activities, selectivities, and stabilities were investigated. The closer the fractional sum of the transition metal electronegativities was to the electronegativity range of the noble catalysts (2.0–2.2), the better was the catalyst performance. The highest diesel selectivity was obtained from NiWC/Al-SBA-15, with a fractional sum of electronegativity of 2.06. The effects of doping a promoter (Ce) on the catalyst electronegativity and activity were studied. Adding Ce generally improved the catalyst performance, by adjusting the combined electronegativities nearer to 2.0–2.2. However, other parameters affected by Ce addition, such as textural properties, or the performance of individual metals could also impact catalyst performance. The NiNbC/Al-SBA-15 catalyst promoted with 5% Ce maintained stable activity for 168 hrs at 400 °C and 4.48 MPa H₂.

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1. Introduction

The search for alternative energy sources that are sustainable and renewable has been motivated by increasing petroleum prices, diminishing fossil fuel reserves, and environmental issues associated with greenhouse gas emissions. Biofuels (in particular, green diesel) produced from the hydroprocessing of vegetable oils typically display properties that are similar to petroleum diesel and can be directly used in existing infrastructures with no modifications [1, 2]. Low quality vegetable oils such as distillers dried grains with solubles (DDGS) corn oil could be appropriate alternatives to fresh vegetable oils as feedstocks because they are inexpensive and non-food-competitive.

During the catalytic hydrocracking of vegetable oils, the triglycerides can be converted to hydrocarbons in the boiling range of diesel as a result of the following reactions [3, 4]:

The hydrogenation reaction dominates initially by converting triglyceride molecules to free fatty acids (FFA), followed by hydrodeoxygenation, hydrodecarboxylation, and hydrodecarbonylation of FFA to green diesel. Supported noble metal catalysts [5] and metal sulfide catalysts [6, 7] have been investigated in the hydrocracking of vegetable oils to produce green diesel. The noble metal catalysts are not viable for the large-scale processes because of their limited availability, high cost, and sensitivity to contaminants (such as oxygenated compounds) in the feedstock [8].

Although metal sulfide catalysts overcome the issues with noble metal catalysts, the addition of sulfur-containing compounds such as H_2S is required to maintain the catalysts in the active form [9].

Recently, supported metal carbide and nitride catalysts have received considerable attention as mediators for the hydrocracking of vegetable oils [10]. The presence of carbon or nitrogen atoms in the transition metal lattice extends the lattice parameter and increases the d-band electron density of the metals [11, 12]. However, only 86% yield of paraffin and 46% selectivity for branched paraffins were obtained from rapeseed oil feedstock when a molybdenum carbide catalyst supported on carbon nanotubes (20% $\text{Mo}_2\text{C}/\text{CNTs}$) was used [13]. Bimetallic carbide and nitride catalysts have shown higher activities and stabilities than the monometallic ones [14]. It has been claimed that the carbide form of the $\text{NiMo}/\text{ZSM-5}$ catalyst produced a lower amount of CO and CO_2 from soybean oil feedstock than the nitride form; therefore, more hydrodeoxygenation took place on the carbide catalyst compared to the nitride catalyst [15]. Most recently, Wang et al. [16] investigated the effect of several supports on the activity of a NiMo carbide catalyst for the hydrocracking of soybean oil. The conversion of soybean oil reached 100% and the selectivity for green diesel was 97% for the NiMo carbide catalyst over Al-SBA-15 during 7 days at 400°C and 4.48 MPa. Our earlier study investigated the effect of catalyst preparation method and Ni-W ratio on the carbide form of the $\text{NiW}/\text{Al-SBA-15}$ catalyst activity and selectivity [17]. The catalyst prepared by Dendrimer-Encapsulated-Nanoparticles (DENP) method with a Ni-W ratio of 2:1 led to a complete conversion of DDGS corn oil for 16 days and 100% diesel selectivity for 4 days at 400°C and 4.48 MPa.

Electronegativity is defined as the tendency of an atom to attract an electron to itself. The ability of the tetrachloroaluminate catalyst to attract and retain hydrocarbon feedstock at the

reaction sites then simultaneously release formed products can be attributed to the electronegativity of the catalyst [18]. According to Sabatier's principle, the maximum rate of catalytic activity is obtained when the rate of reactant adsorption on the catalyst is equal to the rate of product desorption from the catalyst [19]. Nwosu et al. [19] claims that all the noble metals are considered to be good catalysts based on their performance on the Sabatier's volcano scale, and they have almost the same electronegativity. The electronegativity of noble metals is neutral, between the electropositive and electronegative elements; therefore, their ability to adsorb reactants and desorb products is almost equal. Also, this study shows that the closer the electronegativity of transition metals to the range of noble metals (2.0-2.2), the better performance on the Sabatier's volcano scale. However, this study indicates that other factors like particle sizes and synergy pattern hindered the performance of the catalysts. In this respect, noble metal catalysts have shown excellent performance in the hydrocracking of vegetable oils. Since chemical reactions depend on the ability of the reactants to donate, receive, or share electrons; the electronegativity of the material would appear to have a role in this process. For bimetallic catalysts, the ensemble and ligand (electronegativity) effects have the main roles of enhancing the catalyst performance in comparison to monometallic types [20]. The dibenzothiophene conversion for the hydrodesulfurization (HDS) reaction over a Pd-Au bimetallic catalyst was higher than over either Pd or Au alone (84, 16, and 22%, respectively) [21]. Due to the difference in electronegativities between Pd and Au, the sulfur is selectively adsorbed on the Au sites, leaving the Pd sites available for activating hydrogen and accomplishing the HDS reaction.

In the present work, a wet co-impregnation method was used to prepare various catalysts on an Al-SBA-15 support by combining metals with both lower and higher electronegativities, to achieve catalysts with fractional sums of their components' electronegativity values lying in the

electronegativity range of the noble metals. We hypothesized that by mimicking the electronegativity of noble metals, the performance of bimetallic carbide catalysts for the hydrocracking of vegetable oils might improve. The empirical formula used for calculating the fractional sum of the electronegativities of the metals is presented in (eq.1):

$$\vartheta_T = \frac{\sum_i^n \vartheta_i * \varphi_i}{\sum_i^n \varphi_i} \quad (eq.1)$$

where ϑ_T is the electronegativity of the catalyst, ϑ_i is the electronegativity of the individual metal, and φ_i (mol%) is the quantity of the corresponding metal in the catalyst [19]. The effect of the fractional sum of the metals' electronegativities on the activity and selectivity of the catalyst for green diesel production via the hydrocracking of DDGS corn oil was investigated under relatively mild reaction conditions.

2. Experimental

2.1 Materials

Ammonium (*para*)tungstate hydrate ((NH₄)₁₀(H₂W₁₂O₄₂)·4H₂O, 99.99%, Aldrich), ammonium niobate(V) oxalate hydrate (C₄H₄NNbO₉·xH₂O, 99.99%, Aldrich), ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Sigma-Aldrich), zirconium(IV) oxynitrate hydrate (ZrO(NO₃)₂·xH₂O, 99%, Aldrich), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma-Aldrich), and cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.99%, Aldrich) were used as W, Nb, Mo, Ni, and Ce sources, respectively. Carbon disulfide (HPLC grade ≥99.9%), aluminum isopropoxide (C₉H₂₁AlO₃, 99.99%), and the mesoporous silica SBA-15 were purchased from Sigma-Aldrich, Aldrich, and Advanced Chemicals Supplier (ACS), respectively.

2.2. Catalyst preparation

A neutral support, SBA-15, with a 9 nm pore diameter and Brunauer-Emmett-Teller (BET) surface area of 600 m²/g, was modified by aluminum isopropoxide to adjust its acidity. SBA-15 (20 g) was suspended in hexane (150 mL); then, aluminum isopropoxide (0.067 g) was added to the solution and stirred for 24 h. The mixture was filtered, dried, and calcined at 550 °C for 4 h. According to our previous work [17], the catalysts NiNb, NiMo, NiW, and NiZr were prepared in the ratio of 6.67 wt% Ni:3.33 wt% M (M = Nb, Mo, W, Zr) by the wet co-impregnation of aqueous solutions of (Ni(NO₃)₂ · 6H₂O, C₄H₄NNbO₉ · xH₂O), (Ni(NO₃)₂ · 6H₂O, (NH₄)₆Mo₇O₂₄ · 4H₂O), (Ni(NO₃)₂ · 6H₂O, (NH₄)₁₀(H₂W₁₂O₄₂) · 4H₂O), and (Ni(NO₃)₂ · 6H₂O, ZrO(NO₃)₂ · xH₂O) on the modified Al-SBA-15 support. The resulting solids were dried and calcined at 450 °C for 4 h. The catalysts promoted with Ce were prepared by impregnation of the NiNb/Al-SBA-15, NiMo/Al-SBA-15, NiW/Al-SBA-15, and NiZr/Al-SBA-15 catalysts with an approximate amount of 10 wt% (Ce(NO₃)₃ · 6H₂O) solution. The impregnated samples were dried and calcined at 450 °C for 4 h.

Carburization was conducted using temperature-programmed reduction (TPR) according to the method of Claridge et al. [22]. Each metal oxide precursor was placed in a quartz tube and subjected to a flow of 20% CH₄/80% H₂ at 30 cm³/min and a heating rate of 10 K/min to 250 °C, followed by 2.0 K/min to 730 °C. The temperature was maintained at 730 °C, the optimal temperature for carbide formation, for 30 min to complete the reaction [22]. After cooling, the catalyst was passivated under a mixture of 1% O₂ in Ar for 1 h to eliminate its pyrophoricity [14] and protect the bulk of the catalyst against deep oxidation [23].

2.3. Material characterization

The BET surface area, Barrett-Joyner-Halenda (BJH) pore size, and pore volume were determined using a Micromeritics model ASAP 2010 surface area analyzer with 99.9% purity nitrogen gas, and the results were collected on a Tristar 3020 analyzer. The samples were degassed at 400 °C at a heating rate of 10 °C/min for 2 h prior to analysis. X-Ray diffraction (XRD) patterns were collected using a Rigaku RU2000 rotating anode powder diffractometer (Rigaku Americas Corporation, TX) with SmartLab Guidance and MDI Jade 8 software at a scan rate of 8 °/min.

2.4. Hydrocracking reaction procedures

2.4.1. Batch reactor

The catalytic hydrocracking conversion of DDGS corn oil was carried out in a 100 mL Hanwoul stirred batch reactor (Geumjeong-dong, South Korea). To investigate the activity of each catalyst, the reactor was loaded with catalyst (2 g) and reduced in situ under a 30 mL/min flow of H₂ for 3 h at 350 °C. The gas flow rate was controlled by a metal-sealed mass flow controller (Brooks, Warren, MI). After cooling to room temperature, DDGS corn oil (50 mL) was fed into the reactor by a pump (Chrom Tech, Series III) at a rate of 5 mL/min for 10 min. The temperature was increased to 350 °C at a rate of 10 °C/min, and the H₂ pressure in the vessel was increased to 4.48 MPa. The oil is mostly liquid at 350 °C and 4.48 MPa. The agitation speed was maintained at 1100 rpm throughout the reaction. A liquid sample was collected every 30 min for analysis. The sample was allowed to phase separated for 12 hours at room temperature and atmospheric pressure.

2.4.2. Flow reactor

This DDGS corn oil hydrocracking reaction was also performed in a BTRS-Jr. system (Autoclave Engineers, PA) that consisted of a fixed bed reactor with an internal diameter of 1.31

cm and a length of 61 cm, a heater, a pressure regulator, and a condenser. The experimental conditions were similar to those from a previous study [15], in which biofuels were produced via the hydrocracking of soybean oil over transition metal carbides and nitrides supported on ZSM-5. The catalyst (2 g) and quartz beads (4.5 g) were loaded in the reactor and reduced under an H₂ flow of 30 STP mL/min at 450 °C for 3 h. The quartz beads were used to dilute the catalyst bed, prevent plugging, and enhance heat and mass transfer. The reaction was carried out at 400 °C and 4.48 MPa. The hydrogen flow was maintained at a constant 30 mL/min and the DDGS corn oil was fed at a liquid hourly space velocity (LHSV) of 1 h⁻¹. The outlet liquid phase was separated from the gas phase via a condenser maintained at room temperature and 4.48 MPa. The collected liquid samples consisted of two phases: organic liquid product (OLP) and aqueous phase. The OLP samples were analyzed qualitatively and quantitatively. The produced jet fuel and green diesel fractions were identified as (C₈–C₁₆) and (C₁₂–C₂₂), respectively.

2.5 Analysis method

The samples of OLP were dissolved in carbon disulfide and analyzed using a Perkin Elmer Clarus 500 gas chromatograph (GC) equipped with a flame ionization detector (FID) and an Elite-Biodiesel 5HT column (Perkin Elmer, N9316690, length: 15 m; internal diameter: 0.31 mm; phase film thickness: 0.10 µm). For triglycerides analysis, the GC oven temperature was programmed as follows: 1 min hold at 80 °C, 30 °C/min ramp to 240 °C, 10 °C/min ramp to 360 °C, and 15 min hold at 360 °C. The detector temperature was maintained at 360 °C. Samples (0.5 µL) were injected into the column with a 10:1 split ratio. For hydrocarbons analysis, the GC oven temperature was programmed as follows: 5 min hold at 35 °C, 10 °C/min ramp to 360 °C, and 15 min hold at 360 °C. The detector temperature was maintained at 370 °C. Samples (0.5 µL) were injected into the column with a 10:1 split ratio.

3. Results and discussion

3.1 Catalyst characterization

The XRD patterns of the nickel carbide catalyst and the nickel-based carbide catalysts with four different metals supported on Al-SBA-15 are shown in Fig. 1. For all the catalysts, the broad peak between $2\theta = 15\text{--}30^\circ$ corresponds to the mesoporous silica. The XRD patterns of the catalysts show three main peaks at $2\theta = 44.6^\circ$, 52.2° , and 76.3° , corresponding to the (111), (200), and (220) diffractions of the Ni particles, respectively [24]. The carbide phases of Mo, Nb, and W can be observed as shown in Fig. 1(b), (c), and (d), respectively. Surprisingly, the carbide phase of Zr was not observed in the XRD pattern (Fig. 1(e)), which suggests that the phase was very well dispersed on the support. SEM-EDAX was used to characterize the catalyst in order to determine Zr and C distributions on the support (Al-SBA-15). Fig. 2 shows that the distributions of Zr and C on the support are well dispersed with no agglomeration observed at any area. Also, Fig. 3 shows that the atomic weight percentages of the Zr (40.01%) and C (59.99%) in the catalyst were close to that in the most stable phase of ZrC [25]. There is no indication of Ni carbide formation, as shown in Fig. 1(a), confirming that Ni metal was easily reduced to form Ni particles, in agreement with the findings of Gajbhiye et al. [26]. Fig. 1(b) and (d) show that NiMoC/Al-SBA-15 and NiWC/Al-SBA-15 are the only catalysts that form alloys, as indicated by the peaks at $2\theta = 47.3^\circ$ and 48.1° , respectively.

Fig. 4 shows the XRD patterns of the catalysts promoted with Ce. The broadening of peaks of the promoted catalysts suggests smaller crystal sizes and higher metal carbide dispersions than the non-promoted catalysts. Moreover, there is a decrease in the intensities of the diffraction peaks as well as the disappearance of some peaks. Therefore, the Ce additive increases the metal dispersion, leading to the formation of more active centers and greater hydrogen adsorption [27,

28]. No peak assignable to a Ce carbide phase is seen in Fig. 4(b), which indicates that the phase either was not formed or the particles were too small to be detected by the XRD technique [29]. The peak corresponding to the Ni-Mo alloy disappeared and that corresponding to Ni-W alloy decreased, which provides another indication of the enhancement in metal dispersion after adding Ce.

The effect of the loading of the Ce promoter on the structure of NiNbC/Al-SBA-15 was also investigated by XRD (Fig. 5). The higher the loading of Ce, the weaker were the peaks in the XRD pattern of NiNbC/Al-SBA-15, and more peaks disappeared ($2\theta = 26.3^\circ$, 35.5° , and 40.8°) as the Ce amount increased. The particle sizes were estimated by using the Debye-Scherrer equation in order to show the extent to which the peaks have broadened. Table 1 indicates that the increasing in the peak broadening was caused by the decreasing in particle size; therefore, the dispersion of NiNbC increases with the increase in Ce content.

The surface area, pore size, pore volume, and average particle size of the catalysts are summarized in Table 2. The surface area and pore size of the catalysts decreased as compared to the Al-SBA-15 support (surface area: $600 \text{ m}^2/\text{g}$; pore size: 9 nm), which could be caused by loss of structure and/or pore blockage [30]. All of the catalysts have relatively high surface areas and suitable pore sizes that would readily allow the diffusion of bulky triglyceride molecules [27]. The BET surface area of the Ce-promoted catalysts increased compared to the non-promoted catalysts, while the average particle size decreased. These results are in accord with the results obtained from the XRD characterization. Table 3 shows that the surface area increases after adding Ce; however, the surface area decreases as the Ce loading increases further. These decreases in surface area as the Ce loading increases suggest that the addition of Ce may block

some pores in the Al-SBA-15 support [31]. Moreover, the average particle size decreases after adding Ce can be attributed to the increase in metal dispersion.

3.2 Hydrocracking of DDGS corn oil

3.2.1. Relationship between nickel-based catalysts, electronegativity, and catalytic activity

The performance of NiMoC/Al-SBA-15, NiZrC/Al-SBA-15, NiNbC/Al-SBA-15, and NiWC/Al-SBA-15 was evaluated for the hydrocracking of DDGS corn oil in a batch reactor at 350 °C and 4.48 MPa. Table 4 shows the typical fatty acid compositions and the elemental analysis of DDGS corn oil. The collected samples were analyzed by GC-FID to determine the DDGS corn oil conversion and the selectivity for diesel; the results are shown in Fig. 6 as a function of time. The 30 min data point corresponds to the time at which the temperature reaches 350 °C. However, hydrocracking had started before the temperature reached 350 °C because the DDGS corn oil conversion at 30 min was more than 30% for all the catalysts. The conversion at time t (C_t) was calculated as:

$$C_t (\%) = 100\% - C_{TG,t} \quad (eq. 2)$$

where $C_{TG,t}$ is the concentration of triglycerides (%) in the OLP determined by GC-FID analysis at time t . There were no significant differences in the conversion of DDGS corn oil for all the catalysts; however, the selectivity for green diesel varied, and the maximum green diesel selectivity (100%) was obtained from NiWC/Al-SBA-15 after 180 min, as shown in Fig. 6 (d).

The green diesel selectivity at time t ($S_{d,t}$) is defined as:

$$S_{d,t} (\%) = \frac{C_{d,t}}{C_{p,t}} * 100 \quad (eq. 3)$$

where $C_{d,t}$ and $C_{p,t}$ are the concentrations of green diesel and OLP at time t , respectively. Although Fig. 6 (a) shows that the diesel selectivity obtained from NiMoC/Al-SBA-15 reached 86% at 150 min, the diesel selectivity dropped to 69% after 3.5 h. The diesel selectivities of the

NiZrC/Al-SBA-15 and NiNbC/Al-SBA-15 catalysts both increased with time; however, NiNbC/Al-SBA-15 reached 90% earlier than NiZrC/Al-SBA-15. The differences in selectivity could be related to the fractional sum of the electronegativities of the metals. The fractional sum of the electronegativities in a catalyst was calculated using (eq. 1), as shown in Table 5. The catalyst producing the highest diesel selectivity, NiWC/Al-SBA-15, has a fractional sum of electronegativities within the electronegativity range of the noble metal catalysts (2.0–2.2), a result in agreement with Nwosu et al. [19]. On the other hand, the other catalysts did not behave the same way. The catalyst with the second highest fractional sum of the electronegativities of metals did not lead to the second highest diesel selectivity. This suggests electronegativity is not the determining factor for activity and selectivity, and the differences in metal compositions, particle size and surface area may also play a role.

3.2.2. Effect of doping 10% Ce on electronegativity and activity of catalysts

To understand the effect of Ce doping on the catalyst performance for the hydrocracking of DDGS corn oil, the reaction was conducted over a catalyst that contained only cerium (CeC/Al-SAB-15). Both the DDGS corn oil conversion and the diesel selectivity obtained from this catalyst were low (Fig. 7), indicating that adding Ce to the catalysts did not significantly contribute to the hydrocracking reaction.

The Ce-promoted hydrocracking reaction of DDGS corn oil over the NiMoC/Al-SBA-15, NiZrC/Al-SBA-15, NiNbC/Al-SBA-15, and NiWC/Al-SBA-15 catalysts was investigated in a batch reactor at 350 °C and 4.48 MPa to examine the effect of 10% Ce doping. Fig. 8 shows that there was a slight increase in the conversion for the promoted catalysts compared to the non-promoted catalysts. However, a significant improvement in the diesel selectivity was obtained with the promoted catalysts, reaching 100%. Indeed, the Ce-promoted NiNbC/Al-SBA-15

catalyst reached 100% diesel selectivity only after 90 min. The improvement in diesel selectivity for the promoted catalysts could be attributed to several factors, including the value of the fractional sum of the electronegativities. This sum increases after catalyst promotion by Ce (Table 5). As mentioned previously, the optimal electronegativity should be noble-metal-like (2.0–2.2) to equalize the rates of reactant adsorption and product desorption [19], and obtain the highest catalytic activity. The Ce-promoted NiWC/Al-SBA-15 catalyst exhibited approximately similar diesel selectivity to the non-promoted one since the fractional sum of the electronegativities in the non-promoted catalyst already approximated that of the noble catalysts. Nevertheless, other catalysts showed greater diesel selectivity as their fractional sums of electronegativities approached 2.0–2.2. Moreover, based on the XRD and BET analysis, metal dispersion and surface area in the promoted catalysts are enhanced which may lead to the formation of more active centers and the adsorption of more hydrogen [27, 28]. These factors may additionally contribute to the improved diesel selectivity of the promoted catalysts.

3.2.3. Effect of Ce loading on electronegativity and catalyst activity

The NiNbC/Al-SBA-15 catalyst was promoted with four different Ce loadings to study the effect of the fractional sum of the electronegativities on the catalytic activity. Table 5 shows that this fractional sum increases as the Ce loading increases. The catalyst with 20% Ce should have exhibited the best performance since its fractional sum of electronegativities fell in the electronegativity range of the noble catalysts; however, the catalyst with 10% Ce displayed higher performance, as shown in Fig. 9 (c) and (d), respectively. The catalyst with 10% Ce reached 88% DDGS corn oil conversion after 210 min whereas only 78% conversion was obtained from the 20% loading. In addition, the diesel selectivity reached 100% for the catalysts with 10 and 20% Ce after 90 min and 120 min, respectively. The variation in the catalyst

performance could be attributed to the opposing effects of the fractional sums of the electronegativities and the textural properties of the catalysts such as surface area and particle size. Therefore, the enhancement of the catalyst performance due to the electronegativity could be limited by the decrease in surface area and increase in particle size, as shown in Table 3. The diesel yield of the Ce-promoted and non-promoted catalysts was calculated as shown in Table 6. The diesel yield was observed to increase with time, with the catalyst (NiNbCeC/Al-SBA-15 with 10% Ce) achieving the highest diesel yield (88.4%) after 210 min. Based on the hydrogenation reaction, the maximum hydrocarbon gas (propane) produced could be as high as 13% for complete conversion. As indicated from Table 6, total liquid product (weight %) from each catalyst was about 90%.

3.2.4. Catalyst stability

The stability of the NiNbC/Al-SBA-15 catalyst promoted with 5% Ce was investigated in a continuous flow reactor at 400 °C and 4.48 MPa. The conversion of DDGS corn oil over seven days of operation is shown in Fig. 10. The catalyst was stable over the entire duration. The selectivity for jet fuel was higher than for diesel, perhaps due to the higher temperature, which favors higher cracking activity. During the first day, the jet fuel selectivity was 85%, with no production of diesel. The jet fuel selectivity decreased as the diesel selectivity increased with time. This might be due to the retention of deoxygenated and cracked intermediates that are not hydrocracked to produce jet fuel (light HC's); but rather, are retained in the range of diesel because more of the Ni surface is covered by the adsorbed reactants with time [15]. Wang et al. [15] studied the hydrocracking of soybean oil over NiMoC/ZSM-5 at 450 °C and 4.48 MPa and obtained only 42% jet fuel selectivity. The NiNbC/Al-SBA-15 catalyst promoted with 5% Ce

shows greater jet fuel selectivity than NiMoC/ZSM-5 under similar reaction conditions albeit at lower temperature (400 °C).

4. Conclusion

The fractional sum of the electronegativities of the transition metals were correlated with the performance of these catalysts because it affects the reactant adsorption and product desorption steps. The maximum rate of catalytic activity can be obtained when the rates of adsorption and desorption are similar to those observed for the noble metals. It is possible to posit that the closer the fractional sum of the transition metal electronegativities is to the electronegativity range of the noble catalysts (2.0–2.2), the better the catalyst performance will be. However, this is not the only factor that controls the catalyst activity. The BET surface area, particle size, pore size, and metal composition can also affect the activity and selectivity.

Several catalysts were investigated to evaluate the effect of the fractional sum of electronegativity values on the hydrocracking of DDGS corn oil. The catalyst with the fractional sum of electronegativity values in the range 2.0–2.2, NiWC/Al-SBA-15, was the most active. Doping different loadings of Ce brought the electronegativity closer to the 2.0–2.2 range and improved the catalyst performance. However, not every catalyst followed this trend because the improvement obtained from the electronegativity values could be inhibited by other factors, such as surface area and particle size. The NiNbC/Al-SBA-15 catalyst promoted with 5% Ce was studied in a fixed bed reactor over 7 days and achieved high conversions of triglycerides and free fatty acids. Thus, this promoted catalyst may be regarded as a prospective hydrocracking catalyst for inexpensive feedstocks such as brown grease.

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List of Table Captions:

Table 1: Effect of Ce loading on particle size

Table 2: Textural properties of non-promoted catalysts and promoted catalysts with 10% Ce

Table 3: Effect of Ce loadings on textural properties of catalysts

Table 4: Fatty acid compositions and elemental analysis of DDGS corn oil

Table 5: Values of the fractional sum of transition metal electronegativities in the non-promoted and Ce-promoted catalysts

Table 6: Diesel yield and total liquid product weight percentage

Table 1

		Particle size (nm)						Mean crystallite size (nm)
Catalyst	2 θ (°)	22.9	28.3	36.4	44.6	52.2	76.3	-
	NiNbC 0% Ce	33	27	31	29	23	24	27
	NiNbC 5% Ce	31	21	28	18	15	18	19
	NiNbC 10% Ce	29	19	25	17	14	17	16
	NiNbC 20% Ce	28	16	23	17	13	15	15

Table 2

	Non-promoted			
Catalyst	S_{BET} (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	Avg. particle size (nm)
NiWC/Al-SBA-15	342	7.32	0.66	21.3
NiMoC/Al-SBA-15	302	5.85	0.43	17.5
NiNbC/Al-SBA-15	343	5.89	0.48	19.8
NiZrC/Al-SBA-15	299	5.98	0.48	16.9
	Promoted with 10% Ce			
Catalyst	S_{BET} (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	Avg. particle size (nm)
NiWC/Al-SBA-15	388	5.36	0.54	15.4
NiMoC/Al-SBA-15	454	5.84	0.59	13.2
NiNbC/Al-SBA-15	402	6.07	0.55	14.9
NiZrC/Al-SBA-15	353	6.10	0.43	15.1

S_{BET} : BET surface area

Table 3

NiNbCeC/Al-SBA-15	S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Avg. particle size (nm)
0% Ce	343	5.89	0.48	19.8
5% Ce	424	5.4	0.55	14.1
10% Ce	402	5.44	0.53	14.9
20% Ce	346	5.38	0.45	17.3

S_{BET}: BET surface area

Table 4

Fatty acid composition wt.%		Element analysis (ppm)	
C14:0	0.1	Fe	0.4
C16:0	5.8	Na	3.9
C16:1	0.1	Ca	0.2
C18:0	2.5	P	1.8
C18:1	31.3	S	27.6
C18:2	49.1		
C18:3	4.8		
C20:0	3.7		
C22:1	2.6		

Table 5

	Fractional sum of electronegativity values (ϑ_T)			
Catalyst	Non-promoted		Promoted with 10% Ce	
NiZrC/Al-SBA-15	1.72		1.83	
NiNbC/Al-SBA-15	1.81		1.92	
NiMoC/Al-SBA-15	1.99		2.10	
NiWC/Al-SBA-15	2.06		2.17	
Catalyst	0% Ce	5% Ce	10% Ce	20% Ce
NiNbC/Al-SBA-15	1.81	1.87	1.92	2.03

Table 6

	Diesel Yield (%)							
Non-promoted catalyst	30 min	60 min	90 min	120 min	150 min	180 min	210 min	Liquid product wt. (%)
NiMoC	35.4	36.5	34	52.7	59.8	48.3	49.7	86
NiZrC	15.5	25	25.5	28.4	31.9	41.4	62.6	89
NiNbC	12.4	14.8	24.9	27.6	53.7	55.2	59.8	87
NiWC	21.8	24.2	31.1	42.8	48.9	71.9	73.2	89
Promoted catalyst								
NiMoCeC (10% Ce)	21	26.4	40.3	50.7	58.4	62.1	78.3	93
NiZrCeC (10% Ce)	15.9	21.2	30.4	34	37.7	50.9	61.8	83
NiNbCeC (5% Ce)	25.1	26.1	36.6	51.4	67.3	70	71.9	92
NiNbCeC (10% Ce)	18	19.6	51.5	64.3	68.6	71.9	88.4	95
NiNbCeC (20% Ce)	19.2	20.4	28.9	69.3	75.2	76.1	78.6	93
NiWCeC (10% Ce)	22.1	31.6	35.4	37.8	56.1	68.3	78.4	92

List of Figure Captions:

Fig. 1. XRD patterns of NiC/Al-SBA-15 (a), NiMoC/Al-SBA-15 (b), NiNbC/Al-SBA-15 (C), NiWC/Al-SBA-15 (d), NiZrC/Al-SBA-15 (e).

Fig. 2. The distribution of Zr and C in the NiZrC/Al-SBA-15 catalyst: Zr (a) and C (b).

Fig. 3. EDAX spectra of NiZrC/Al-SBA-15 catalyst.

Fig. 4. XRD patterns of (10% Ce) NiC/Al-SBA-15 (a), CeC/A-SBA-15 (b), (10% Ce) NiMoC/Al-SBA-15 (C), (10% Ce) NiNbC/Al-SBA-15 (d), (10% Ce) NiWC/Al-SBA-15 (e), (10% Ce) NiZrC/Al-SBA-15 (f).

Fig. 5. XRD patterns of the promoted NiNbC/Al-SBA-15 catalyst with: 0% Ce (a), 5% Ce (b), 10% Ce (c), 20% Ce (d).

Fig. 6. DDGS corn oil conversion and diesel selectivity in batch reaction at 350 °C and 650 psi on NiMoC/Al-SBA-15 (a), NiZrC/Al-SBA-15 (b), NiNbC/Al-SBA-15 (C), NiWC/Al-SBA-15 (d).

Fig. 7. DDGS corn oil conversion and diesel selectivity in batch reaction at 350 °C and 650 psi on CeC/Al-SBA-15.

Fig. 8. DDGS corn oil conversion and diesel selectivity in batch reaction at 350 °C and 650 psi on Ce promoted catalysts with (10% Ce): NiMoC/Al-SBA-15 (a), NiZrC/Al-SBA-15 (b), NiNbC/Al-SBA-15 (C), NiWC/Al-SBA-15 (d).

Fig. 9. DDGS corn oil conversion and diesel selectivity in batch reaction at 350 °C and 650 psi on Ce promoted NiNbC/Al-SBA-15 catalyst with: 0% Ce (a), 5% Ce (b), 10% Ce (c), 20% Ce (d).

Fig. 10. DDGS corn oil conversion and diesel selectivity in flow reaction with liquid hourly space velocity (LHSV) of 1 h^{-1} at $400 \text{ }^{\circ}\text{C}$ and 650 psi on Ce promoted NiNbC/Al-SBA-15 catalyst with 5% Ce.

Fig. 1.

(a)

(b)

Fig. 2

Fig. 3

Fig. 4.

Fig. 5.

(a)

(b)

(c)

(d)

Fig. 6.

Fig. 7.

(a)

(b)

(c)

(d)

Fig. 8.

(a)

(b)

(c)

(d)

Fig. 9.

Fig. 10.

Hydrocracking of DDGS Corn Oil, 350 °C, 4.48 MPa

Fractional Sum of Metal
Electronegativities

$$\vartheta_T = \frac{\sum_i^n \vartheta_i * \varphi_i}{\sum_i^n \varphi_i} = (2.0 - 2.2)$$