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Effect of Keggin type heteropolyacids on hydrocracking of Jatropha oil

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Abstract

To investigate the effect of Keggin type heteropolyacids on hydrocracking of Jatropha oil, the Ni-heteropolyacids/nano-hydroxyapatite (Ni-HPAs/nHA) catalysts were prepared with different Keggin type heteropolyacids loading: phosphotungstic acid (HPW), phosphomolybdic acid (HPMo), silicotungstic acid (HSiW) and silicomolybdic acid (HSiMo). The catalysts were characterized by N_2 adsorption-desorption, powder X-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), temperature programmed desorption of ammonia (NH_3-TPD) and thermogravimetric analysis (TGA), their acidity at reaction temperature (360°C) were determinated by solid-state ^{1}H nuclear magnetic resonance (^{1}H NMR), the acidity order of catalysts at reaction temperature was as follows: HSiW>HPW>HSiMo>HPMo. The Jatropha oil and hydrocracking product oil were analysed by liquid-state ^{13}C nuclear magnetic resonance (^{13}C NMR). The hydrocracking conversions of Jatropha oil over these Ni-HPAs/nHA catalysts were 100%, the highest *Iso*/*n*-alkane ratio was 1.64 and lowest pour point of product oil was -32°C at 360°C, 3MPa, H_2/oil (v/v) =600 and LHSV=2 h^{-1} over Ni-HSiW/nHA catalyst. The results demonstrated the Keggin type heteropolyacids could improve the conversion of Jatropha oil, the isomerization of hydrocracking was affected by the acidity of heteropolyacids at reaction temperature and stronger acidity could produce more *iso*-alkanes.

Keywords: Ni-HPAs/nHA, Jatropha oil, Hydrocracking, isomerization, NMR

Introduction

Biofuels, as the promising renewable and sustainable alternative fuels for replacement of limited fossil fuels have attracted a lot of attentions. [1-3] Among current production techniques of biofuel, hydrocracking of vegetable oil plays an important role from an economic point of view. [4, 5] Its production has similar components with fossil fuels. Moreover, it contains few sulphur and nitrogen compounds. [6, 7] As a consequence, this kind of biofuel shall reduce the more concerned environment pollution and the greenhouse effect. Therefore, there are essential needs for hydrocracking of vegetable oil.

Traditional catalysts for hydrocracking were nickel-based catalysts, the sulfurated nickel and other assisted metal (W and Mo) were loaded into catalyst support (Al_2O_3 and SiO_2). [5, 8, 9] However, during the hydrocracking processing, the sulfur-contained product oil and H_2S gas emission would lead contamination to the environment. [10, 11] On the other hand, the main content of the product oil was the *n*-alkane, which has relative high pour point, its low temperature fluidity limited the application. [12, 13] Since the low temperature fluidity of biofuel can be improved by

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increasing the content of *iso*-alkane, some research have focused on the isomerization of *n*-alkane. For examples, the NiW/SiO_2-Al_2O_3 and Pt/SAPO-11were used for hydrocracking of *n*-decane. [14, 15] On previous work, [16] we have found the nano-hydroxyapatite (nHA) support with phosphotungstic acid loading could get rid of sulphur and increase the *iso*-alkane content to lower the pour point in hydrocracking of Jatropha oil, demonstrating the Keggin type heteropolyacids (HPAs) have potential to be the promising catalysts for hydrocracking. Due to their unique physicochemical properties are widely used as homogeneous and heterogeneous acid and oxidation catalysts, it is necessary to make detailed research of Keggin type heteropolyacids.

According to the classical carbenium ion theory, [17] the isomerization of hydrocracking process is due to the formation of carbenium ion intermediates which require the proton donator, thus the acidity of catalyst becomes one of the key factor for isomerization. The acidity of bifunctional catalysts were provided by the support (HY, HZSM and SAPO), many research demonstrated both acidity and structure of catalyst support affect the isomerization. [18, 19] Being used in catalysis, the Keggin type heteropolyacids have significantly higher Brønsted acidity for isomerization, compared with other type heteropolyacids, the Keggin type heteropolyacids are thermally more stable. [20, 21] However, the results of Thomas et al stated the acidity of phosphotungstic acid can be changed by high temperature variation. [22] Thus in this work, the Keggin type heteropolyacid, including phosphotungstic acid (HPW), phosphomolybdic acid (HPMo), silicotungstic acid (HSiW) and silicomolybdic acid (HSiMo) shall be loaded into nickel based nHA for hydrocracking of Jatropha oil, avoiding the interference of catalyst structure. To approaching the catalyst state of reaction, the solid-state ^{1}H NMR was applied to simulate the acidity of catalyst at reaction temperature (360°C). The different hydrocracking results of Ni-HPAs/nHA catalysts were also compared and discussed.

Experimental

Catalyst preparation and characterization

The nHA was prepared by a precipitation method. [23] All the chemical reagents used in this work were analytic reagent and purchased from Sinopharm Chemical Reagent Co., Ltd, China. $Ca(NO_3)_2\cdot 4H_2O$ was dissolved in deionized water. Then the $Na_3PO_4\cdot 6H_2O$ were dissolved in deionized water to obtain Na_3PO_4 solution, the Na_3PO_4 solution was titrated into the blend solution at a Ca/P molar ratio of 1.67 with mechanical stirred and ultrasonic processing at pH 10 under room temperature. After that, the stirring was continued for 1 h with ultrasonic and kept the slurry aged for 12 h, then washed with deionized water to pH 7. The obtained precipitate after centrifugation was calcined at 400°C for 6 h.

Then, the Ni-HPAs/nHA catalysts were prepared by impregnation of aqueous solutions of $Ni(NO_3)_2\cdot 6H_2O$, and impregnated of aqueous solutions of heteropolyacid. Impregnated samples were dried at 105°C over night and calcined at 200°C for 6 h. The obtained catalyst samples were Ni-HPW/nHA, Ni-HPMo/nHA, Ni-HSiW/nHA and Ni-HSiMo/nHA, respectively. We set the HPW loading amount 30% (which was confirmed as the suitable HPW loading amount for hydrocracking by our previous work) as a reference. [16] To guarantee the different catalyst samples had the same mole number of heteropolyacid for comparison, different heteropolyacid loading amount was as follows: $H_3PW_{12}O_{40}$ (30 wt%), $H_3PMo_{12}O_{40}$ (19 wt%), $H_4SiW_{12}O_{40}$ (30 wt%) and $H_4SiMo_{12}O_{40}$ (19 wt%), the Ni loading amount was 5 wt%.

N_2 adsorption-desorption was measured to determine specific surface areas and pore size distributions, using a V-Sorb 2800 TP Surface Area and Pore Distribution Analyzer instrument

(BeiJing Gold APP Instruments Co., Ltd). The Ni-HPAs/nHA catalysts samples were degassed in a vacuum at 300°C for 2 h before the measurements. Specific surface area was determined by the Brunauer, Emmett and Teller (BET) procedure. The area of the micropores and Pore size distribution (pore diameter and pore volume) were respectively determined by the t-plot method and Barret-Joyner-Halenda (BJH) method from the adsorption branch of the isotherms.

X-ray diffraction (XRD) patterns were carried out using Cu-Kα radiation at 40 kV and 30 mA, recording on a D/max2500VB2+/PC XRD analyzer (Japan Electronics Science Co.,Ltd.). The Ni-HPAs/nHA catalysts samples were measured in the 2θ range from 10° to 80° at a scan speed of 2°/min.

The metal state of Ni-HPAs/nHA catalysts samples was determined by X-ray photoelectron spectroscopy (XPS) measurements, using a ESCALAB 250Xi instrument (Thermofisher) at 280 eV pass energy. Binding energies were corrected for sample charging using the C 1s peak at 284.6 eV for adventitious carbon as a reference.

The acidities of the Ni-HPAs/nHA catalysts samples were determined by temperature programmed desorption of ammonia (NH_3-TPD) using a DAS-7000 Multi-functional automatic Adsorption Instrument (Beijing surface technology Co., Ltd). All samples were pretreated in He (25 mL/min) at 300°C for 2 h. After adsorption of ammonia, the desorption step was performed at a heating rate of 10 °C/min from 100°C to 700°C.

These Ni-HPAs/nHA catalysts samples were also studied by solid-state ^{1}H NMR (Switzerland Burker AVANCE III nuclear magnetic resonance spectrometer) as a function of the temperature of 20°C and 360°C (which was confirmed as the suitable reaction for hydrocracking by our previous work). [16] The Ni-HPAs/nHA catalysts powder (200 mg) was treated under vacuum at the temperature of 20°C and 360°C for 2 h in a sealed ampoule. In order to achieve relatively quantitative results, all ^{1}H NMR spectra were recorded at the same time. The ampoule, which was containing the Ni-HPAs/nHA catalysts samples, was broken in a glovebox, then the rotor was filled and tightly closed by using a cap. The catalyst sample's amount was determined by weighting the rotor before and after it being filled. The NMR spectrum was recorded on a spectrometer operating at 300.13 MHz, the spinning rate was 10 kHz and the eight scans were acquired after a $\pi/2$ pulse. [22]

The amount of coke on the past-reacted catalysts was using thermogravimetric analysis (TGA), performing on a NETZSCH STA449F3 analyzer. Samples were first heated from 30°C to 550°C with a heating rate of 30°C min^{-1} in N_2 flow of 100 ml min^{-1}, at the temperature of 550°C for 15 min, then heated linearly at 30°C min^{-1} to 800°C in 100 ml min^{-1} O_2 flow. The weight loss of samples was calculated by microcomputer.

2.2 Catalytic activity measurements

The Jatropha oil was purchased from Jiangsu Donghu Bioenergy Co., Ltd, including myristic acid (0.8%), arachic acid (0.5%), linolenic acid (0.9%), palmitoleic acid (1.2%), stearic acid (7.3%), palmitic acid (14.8%), linoleic acid (36.2%) and oleic acid (38.3%).

The experiments were performed in a fixed-bed reactor (JF-2, Tianjing Golden Eagle Technology Co., Ltd, China), including feed system, heating section, tubular reactor, condensation section, storage section, instrumentation and control section. The reaction temperature, system pressure and hydrogen input rate was controlled by the microcomputer.

The different catalyst samples (10 g) were loaded into the tubular reactor and activated prior to the experiments with H_2 flow at 400°C and 3 MPa for 3 h. The reaction conditions for catalytic hydrocracking experiment were temperature 360°C, pressure 3 MPa, LHSV 2 h^{-1}, and H_2 to feed ratio of 600 mL H_2 gas/mL liquid feed. [16]

After 8 h of stabilization of reaction conditions, The product oil was analyzed by a gas chromatograph equipped with a flame-ionization detector (FID). The capillary column (AT.SE-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. Normal alkane standards (purchased from Sigma–Aldrich, LLC) were used to estimate the relative percentages and distributions of the product oil with respect to their carbon numbers. The conversion of Jatropha oil was calculated as:

$$C = 100\% - C_{(T)} \quad (1)$$

where $C_{(T)}$ is the concentrations of Jatropha oil (%) in the product oil determined by GC analysis.

The *n*-alkane and *iso*-alkane were calculated on the basis of GC analyzer program data on microcomputer. To value the low temperature fluidity, the pour point of product oil was determinated (based on ASTM D97-93) by a pour point tester (Normalab, model NTE 450, France). To analyse the chemical component of Jatropha oil and liquid hydrocracking products, the ^{13}C NMR spectra for liquid products were recorded by a Varian (USA) INOVA 500 NMR spectrometer operating at a frequency of 125 MHz, using a 5 mm inverse Z-gradient vitreous probe.

Results and discussion

Characterization of catalyst

The Pore size distribution and nitrogen adsorption-desorption isotherms of different catalysts samples were presented in Fig. 1. The pore size distribution of nHA was mainly ranging from 5 to 50 nm, belonging to the mesoporous. Based on the literature, the mesoporous material support was supposed to be appropriate for the catalysis of macromolecule, such as Jatropha oil. All catalysts samples increased gradually as the relative pressure increased and then increased rapidly at high relative pressure ($P/P^0 > 0.4$), in agreement with the literature. [24]After impregnation, the total adsorption of the samples had no obvious change. As shown in Table 1, the nHA also exhibited large specific surface areas (109 m^2/g) and total pore volume (0.51 cm^3/g). After impregnation, the specific surface areas of and total pore volume of catalysts samples increased while the average pore diameter slightly decreased, suggesting that some of the pores were blocked by the metal and heteropolyacids.

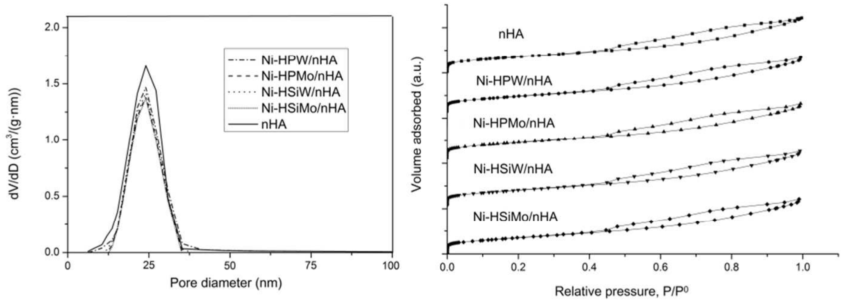

Fig. 1 Pore size distribution and nitrogen adsorption-desorption isotherms of catalysts samples

Table 1 Textural properties of catalysts samples

Catalyst	Specific surface areas, m^2/g	Total pore volume, cm^3/g	Average pore diameter, nm
nHA	109	0.51	22

Ni-HPW/nHA	97	0.47	20
Ni-HPMo/nHA	98	0.46	20
Ni-HSiW/nHA	96	0.48	20
Ni-HSiMo/nHA	99	0.46	20

The XRD pattern of different catalysts samples were shown in Fig. 2. All catalysts samples exhibited the same characteristic peaks of nHA at 2θ = 25.8°, 31.9°, 39.8°, 46.7° and 49.5° respectively. [25, 26] After Ni loading, the character peaks of Ni oxide phase were observed at 2θ = 37.3°, 43.6°, and 63.4°. [23, 27] Then, after these heteropolyacids loading, in each of the ranges of 2θ = 16~23°, 25~30° and 31~38°, the catalysts samples showed characteristic peaks of heteropolyacids having Keggin structure. [28]

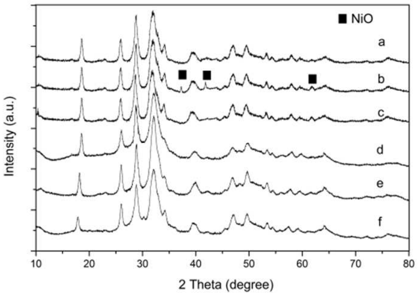

Fig. 2 XRD patterns of (a) nHA, (b) Ni/nHA, (c) Ni-HPW/nHA, (d) Ni-HPMo/nHA, (e) Ni-HSiW/nHA and (f) Ni-HSiMo/nHA

In our previous work, [16] we had proved that the phosphotungstic acid could lead the Ni^{2+} to Ni^0, which would contribute to the enhancement of hydrogenation activity, the same result was also reported by Zheng et al. [29] To investigate whether the state of Ni was caused by other heteropolyacids, different catalysts samples were examined using X-ray photoelectron spectroscopy (XPS). The Ni 2p core level signal of the catalyst was shown in Fig. 3, the binding energy values at 851.4 and 852.1 eV were associated with the Ni^0 of Ni/nHA and Ni-HPAs/nHA catalysts respectively, other peaks were associated with the Ni^{2+}. [30] It was obvious that all heteropolyacids had reducing capacity, being able to increase the amount of Ni^0. Based on the reported literature, [31, 32] the reduction state of metal was able to promote the activity of hydrogenation, thus the conversion of Jatropha oil was improved.

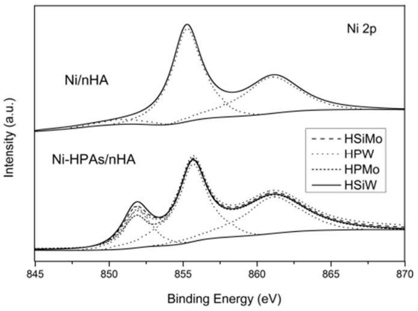

Fig. 3 XPS spectra of Ni 2p levels of catalysts samples

The NH_3-TPD profiles of Ni-HPAs/nHA catalysts with different Keggin type heteropolyacid loading were shown in Fig. 4, the total acidity of the catalysts were recorded in Table 2. The nHA support only represented a small peak around 200°C, after heteropolyacids loading, all Ni-HPAs/nHA catalysts exhibited two broad peaks around the 200°C and 450°C. These results illustrated that the Keggin type heteropolyacid loading increase the acidity (including weak and strong acidity) of the catalyst, offering the acid sites for the catalysis, then as the proton source, the heteropolyacid could promote the isomerization process of hydrocracking. [14, 33] However, different kind of Ni-HPAs/nHA catalysts also represented difference of acidity, it can be seen from the Table 2, the order of acidity was: HPW>HSiW>HPMo>HSiMo, in accord with the reported literature. [20, 28]

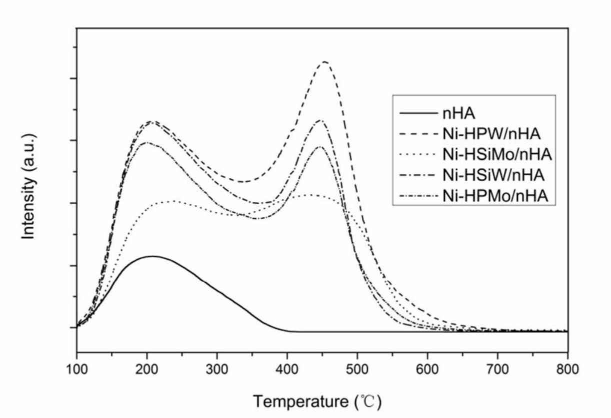

Fig. 4. NH_3-TPD profiles of Ni-HPAs/nHA catalysts with different Keggin type heteropolyacid loading

Table 2 Acidity of Ni-HPAs/nHA catalysts with different Keggin type heteropolyacid loading

Catalyst	Total acidity (mmol/g)
nHA	0.11
Ni-HPW/nHA	0.81
Ni-HSiW/nHA	0.65
Ni-HPMo/nHA	0.52
Ni-HSiMo/nHA	0.43

To investigate the acidity of the catalyst at the hydrocracking reaction temperature (360°C), the solid-state ^1H NMR was used. The Fig. 5 showed the ^1H NMR spectra of these Ni-HPAs/nHA catalysts samples as a function of temperature at 20°C and 360°C. In every case of signal, the spectra exhibited two main peaks, one is sharp at around 0 ppm represented the structural hydroxyl group of nHA, [34] another broad resonance between 2.5 and 15 ppm were corresponding to the protons of heteropolyacids. [35] After integration of the relative peak area of Ni-HPAs/nHA catalysts, we set the area of HPW and hydroxyl group in Ni-HPW/nHA at 20°C as 100%, then the profile was recorded in Table 3. It was obvious that at the 20°C, the order for proton amount of these Ni-HPAs/nHA catalysts samples were in agreement with the NH_3-TPD profiles. At the 360°C, the signal of nHA's hydroxyl group almost remained the same, illustrating the reaction temperature had no effect on the acidity of nHA support. However, there was a reduction amount for all heteropolyacids' proton. Besides, the HPW and HPMo lost more protons than HSiW and HSiMo, the new order of the acidity at 360°C was as follows: HSiW>HPW>HSiMo>HPMo.

These results demonstrated the acidity of Keggin type heteropolyacid was affected by the high temperature, the structure of heteropolyacids was probably changed or damaged, and that the heteropolyacid whose heteroatom was silicon had better high temperature resistance than the heteropolyacid whose heteroatom was phosphorus. The influence of Ni-HPAs/nHA catalysts acidity's variation for hydrocracking results shall be discussed later.

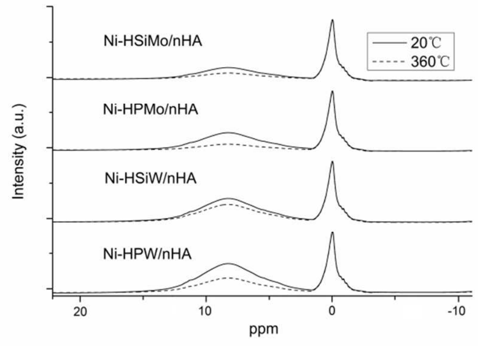

Fig. 5 Solid-state ^{1}H NMR spectra of Ni-HPAs/nHA catalysts with different Keggin type heteropolyacid loading at 20°C and 360°C

Table 3 Relative peak area of HPAs and hydroxyl group in Ni-HPAs/nHA catalysts with different Keggin type heteropolyacid loading

Catalyst	Relative peak area of HPAs (%)		Relative peak area of hydroxyl group (%)	
	20°C	360°C	20°C	360°C
Ni-HPW/nHA	100	51.8	100	100
Ni-HSiW/nHA	81.6	63.3	100	100
Ni-HPMo/nHA	64.1	24.8	100	100
Ni-HSiMo/nHA	48.7	32.5	100	100

According to the reference of ISO 6964-1986, the amount of carbonaceous deposition (coke) on the used catalysts were determined by TGA. As shown in Fig. 6, the amount of coke on these Ni-HPAs/nHA catalysts samples after use for 8 h was significantly different, following the order: HSiW>HPW>HSiMo>HPMo. On the other hand, after use for 148 h, the amount of coke on these Ni-HPAs/nHA catalysts samples was also different, increasing 0.71%, 0.65%, 0.44% and 0.43% than 8 h, respectively. Based on the literature, the coke of hydrocracking catalyst was relating with the acidity of catalyst, which could donate the proton for the coke formation. [36-38] Therefore, stronger the acidity of catalyst was, more coke obtained.

As the ^{1}H NMR spectra had confirmed, the acidities of these Ni-HPAs/nHA catalysts samples at 360°C reduced, that would explain the coke amount on theses catalysts was not as much as the reported literature, whose reaction temperature was lower than 360°C. [39, 40] Especially for the HPW and HPMo, their acidity were significantly influenced by the high temperature, limiting their capacity of proton donation. Therefore, the coke amount of these Ni-HPAs/nHA catalysts samples after use for 8 h and 148 h was in the same order with catalysts' acidities at 360°C.

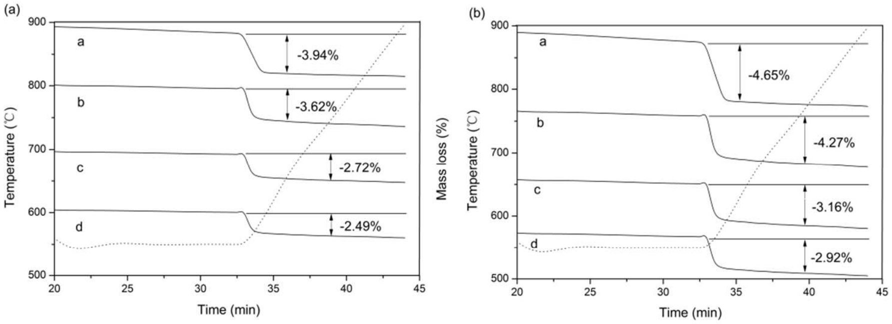

Fig. 6 TGA profiles of a.Ni-HSiW/nHA b.Ni-HPW/nHA c.Ni-HSiMo/nHA d.Ni-HPMo/nHA after use for (a) 8 h and (b) 148 h at 360°C, 3MPa, H_2/oil (v/v) = 600, LHSV=2 h^{-1}

Hydrocracking of Jatropha oil

The GC charts of the product oil from hydrocracking of Jatropha oil over different catalysts samples at 360°C, 3MPa, H_2/oil (v/v) =600, LHSV=2 h^{-1} were shown in Fig. 7, the main products were alkanes (including *iso*-alkane and *n*-alkane) ranging from C15~C18. [16] The distribution of product oil were shown in Fig. 8, it was obvious that the distribution of product oil were significantly influenced by different Ni-HPAs/nHA catalysts. After heteropolyacid loading, the GC charts and distribution of product oil all confirmed that the contents of the diesel range alkanes (C10~C20) and gasoline range alkanes (<C10) [41] had close relationship with the acidity of the Ni-HPAs/nHA catalysts at 360°C, the Ni-HSiW/nHA catalyst lead more gasoline range alkanes and less diesel range alkanes, while the Ni-HPMo/nHA lead more diesel range alkanes and less gasoline range alkanes.

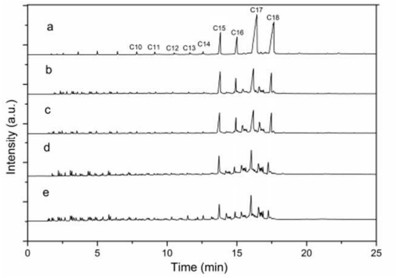

Fig. 7 GC charts of liquid products over (a) Ni/nHA (b) Ni-HPMo/nHA (c) Ni-HSiMo/nHA (d) Ni-HPW/nHA (e) Ni-HSiW/nHA at 360°C, 3 MPa, H_2/oil (v/v) =600, LHSV=2 h^{-1}

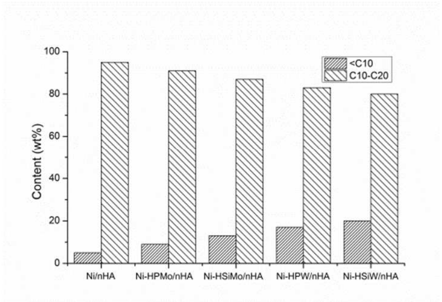

Fig. 8 Distribution of product oil over different catalysts samples at 360°C, 3 MPa, H_2/oil (v/v) = 600, LHSV=2 h^{-1}

The process of hydrocracking of Jatropha oil was shown in Fig. 9. [16, 41] Chemically, 3 mole fatty acid shall be produced from 1 mole of raw materials (triglycerides). As the literature had proved that after the oxygen removing reaction in hydrogen atmosphere, the fatty acid transformed to alkane. There are two routes of the oxygen removing, one is hydrodeoxygenation (HDO), whose product was even carbon number alkanes (mainly C16 and C18) and H_2O; the other is hydrodecarboxylation (HDC), including decarbonylation and decarboxylation, whose product was odd carbon number alkane (mainly C15 and C17) and CO, CO_2. Regardless of reaction condition, this reaction was mainly due to the hydrogenation capacity, which mainly depend on the metallicity of catalyst.

After that, the isomerization process of alkanes shall happen by the cooperation of metal and acid sites, [42] for the catalysts of this research, they were offered by the Ni and heteropolyacids. According to the classical carbenium ion principle, the isomerization process was as follows: I. Through hydride elimination, the *n*-alkane shall transforme to *n*-olefin. II. The carbenium ion intermediates was formed by proton addition. III. The formed normal carbenium ion intermediates isomerized to abranched carbenium ion intermediates. IV. The *Iso*-olefin was formed by eliminating proton of carbenium ion intermediates. V. Through hydrogenation, the *iso*-olefin transformed to *iso*-alkane. The metal sites achieved step 1 and 5, while the acid sites achieved other steps. Therefore, as the GC charts illustrated (see Fig. 7), the main contents of product oil were *n*-alkanes and *Iso*-alkanes ranging from C15~C18. However, at the step 3, the carbenium ion intermediates still had a possibility to crack. If the cracking reaction was enhanced, more gasoline range alkanes will be obtained.

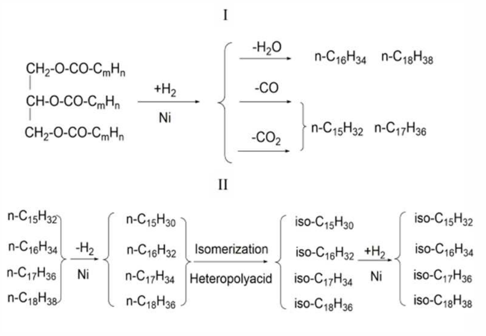

Fig. 9 The process of hydrocracking of Jatropha oil

The properities of product oil obtained by hydrocracking of Jatropha oil over Ni-HPAs/nHA catalysts with different heteropolyacid loading at 360°C, 3MPa, H_2/oil (v/v) =600, LHSV=2 h^{-1} were shown in Table 4. All Ni-HPAs/nHA catalysts had the similar function of improving the catalytic activity of hydrocracking, their conversions achieved 100%. Based on the characterization data of XPS and NH_3-TPD, the heteropolyacid increased the content of Ni^0 and offered protons for isomerization, therefore the hydrocracking activity was improved and more *iso*-alkanes were obtained. [14, 31-33, 43] Through the comparison of different Ni-HPAs/nHA catalysts, it was obvious that the Ni-HSiW/nHA catalyst produced more *iso*-alkanes, achieving the highest *Iso*/*n* ratio (1.78) and lowest pour point (-32℃). The *Iso*/*n* ratio order was the same with the acidity of these catalysts at 360°C. Based on the ^{1}H NMR and the results reported by Zhang et al., [44] the increased acidity of the catalyst shall lead to more formation of carbenium ion intermediates, enhancing both isomerization and cracking, eventually producing more *Iso*-alkanes and gasoline range alkanes, the profiles of product oil distribution and *Iso*/*n* ratio were in agreement with it. Besides, the ratio of $(C_{15}+C_{17})/(C_{16}+C_{18})$ also increased, almost had a linear correlation with the acidity of catalyst, suggesting the strong acidity tend to HDC route.

Table 4 Hydrocracking of Jatropha oil over Ni-HPAs/nHA catalysts with different heteropolyacid loading at 360°C, 3MPa, H_2/oil (v/v) =600, LHSV=2 h^{-1}

Catalyst	Conversion (%)	$(C_{15}+C_{17})/(C_{16}+C_{18})$	*Iso*/*n* ratio	Pour point (□)
Ni/nHA	84.6	1.1	0.3	10
Ni-HPMo/nHA	100	2.2	1.41	-18
Ni-HSiMo/nHA	100	2.8	1.52	-23
Ni-HPW/nHA	100	4.4	1.64	-28
Ni-HSiW/nHA	100	4.8	1.78	-32

The ^{1}H NMR spectra was able to analysis the variation of acidity for the Ni-HPAs/nHA catalysts at the reaction temperature (360°C), consequently the results (*Iso*/*n* ratio and distribution of product oil) of these Ni-HPAs/nHA catalysts were different from other experiment results with relative low reaction temperature. [33, 40] This result was also meaningful for the catalysis of heteropolyacids catalysts used at the high temperature conditions. Moreover, different distribution of product oil can be obtained by different heteropolyacid loading, fulfilling different needs.

Analyses of liquid products

To analyses the chemical changes of the Jatropha oil and the product oil of hydrocracking, the liquid-state ^{13}C NMR was used. The ^{13}C NMR profiles of Jatropha oil and products oil obtained over Ni-HPAs/nHA catalysts with different heteropolyacid loading at 360°C, 3 MPa, H_2/oil (v/v) = 600, LHSV=2 h^{-1} were shown in Fig. 10. For Jatropha oil, the existing peaks of fatty acid chain were mainly located at four area: 10~50ppm, 60~80ppm, 120~140ppm and 170~180ppm, corresponding to the C-C, C-O, C=C and C=O. [45, 46] For the product oil of hydrocracking, all peaks were only in the region of alkanes between 10~50ppm, demonstrating the completely conversion of Jatropha oil. Based on the results of Madhiral et al., the content of *n*-alkane was in direct proportion to the integral intensities of the signals in the region 29.5~30 ppm (represent $-(CH_2)_n-$), while the content of *Iso*-alkane was in proportion to the integral intensities of the signals in the region 10~15 ppm (represent $-CH_3$). [47, 48] Then the ratio of $-CH_3$ signal intensities to $-(CH_2)_n-$ could be used for valuing the ratio of *Iso*/*n*-alkane. After integration and calculation, the ratio profiles of $-CH_3/-(CH_2)_n-$ were recorded in Table 5. After comparison of different Ni-HPAs/nHA catalysts, the highest ratio of $-CH_3/-(CH_2)_n-$ was obtained by hydrocracking over Ni-HSiW/nHA catalyst. The $-CH_3/-(CH_2)_n-$ ratio order was in accord with the *Iso*/*n* ratio of hydrocracking, demonstrating the heteropolyacid loading could enhance the isomerization capacity of hydrocracking catalyst.

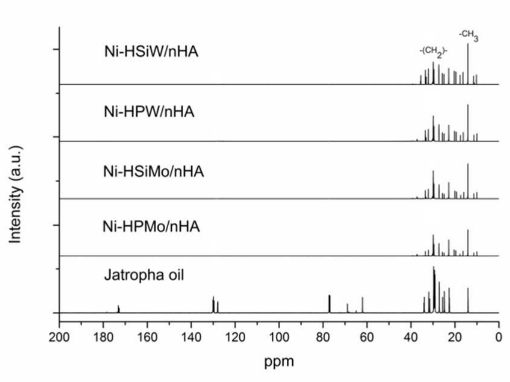

Fig. 10 The ^{13}C NMR profiles of Jatropha oil and product oil obtained over Ni-HPAs/nHA catalysts with different heteropolyacid loading at 360°C, 3MPa, H_2/oil (v/v) = 600, LHSV=2 h^{-1}

Table 5 The ratio profiles of $-CH_3/-(CH_2)_n-$ for Jatropha oil and product oil obtained over Ni-HPAs/nHA catalysts with different heteropolyacid loading at 360°C, 3MPa, H_2/oil (v/v) = 600, LHSV=2 h^{-1}

Catalyst	Ratio of $-CH_3/-(CH_2)_n-$
Jatropha oil	0.18
Ni-HPMo/nHA	0.91
Ni-HSiMo/nHA	1.09
Ni-HPW/nHA	1.18
Ni-HSiW/nHA	1.27

Reaction of time-on-stream

The conversion of Jatropha oil and the ratio of *Iso*/*n*-alkane of product oil over these Ni-HPAs/nHA catalysts samples as a function of reaction time at 360°C, 3 MPa, H_2/oil (v/v)=600, LHSV=2 h^{-1} were shown in Fig. 11. It was obvious that after 8 h, both conversion and *Iso*/*n*-alkane ratio almost remained constant, suggesting the catalytic system reached steady state. After 148 h reaction of time-on-stream, the conversion and ratio of *Iso*/*n*-alkane still remained the same. As the characterization of catalysts and literature all proved, [14, 31-33] the heteropolyacid loading had the capacity of reduction and being the proton source, therefore, that would keep the hydrocracking process stable.

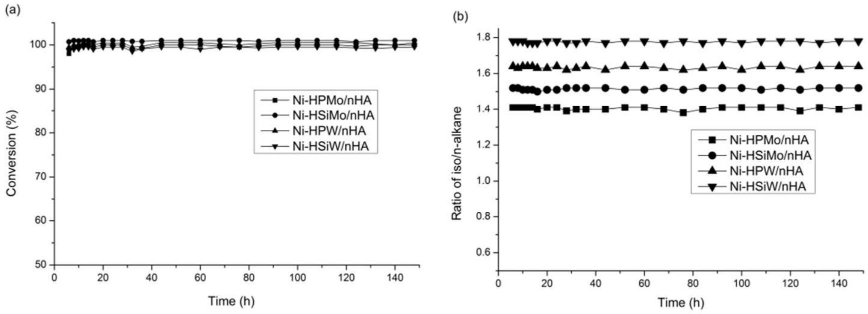

Fig. 11 (a) Conversion of Jatropha oil and (b) ratio of *Iso*/*n*-alkane of product oil over Ni-HPAs/nHA catalysts with different heteropolyacid loading at 360°C, 3MPa, H_2/oil (v/v) = 600, LHSV=2 h^{-1} as a function of reaction time

Conclusion

The effect of four Keggin type heteropolyacids loaded on nHA support for hydrocracking of Jatropha oil were investigated. The heteropolyacids loading could increase the reduction state of Ni and provide protons for isomerization of hydrocracking. As a result, the conversion of Jatropha oil was improved and the isomerization was enhanced. The acidity of catalysts at reaction temperature (360°C) was detected by solid-state ^{1}H NMR, its order was as follows: HSiW>HPW>HSiMo>HPMo. The stronger acidity of heteropolyacids catalyst could provide more protons for the formation of carbenium ion intermediates, promoting the isomerization of hydrocracking. Thus, among these catalysts, the Ni-HSiW/nHA achieved the product oil with highest ratio of *iso*/*n*-alkane (1.78) and lowest pour point (-32°C).

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Graphical Abstract

Textual Information

Description (if any)	The Keggin type heteropolyacids could increase the *iso*-alkane content of product oil obtained by hydrocracking of Jatropha oil
Title	Effect of Keggin type heteropolyacids on hydrocracking of Jatropha oil
Authors' Names	Kai Fan, Jing Liu, Xiaoyi Yang, Long Rong*

Graphical Information