



High quality diesel-range alkanes production via a single-step hydrotreatment of vegetable oil over Ni/zeolite catalyst



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ARTICLE INFO

Article history:

Received 18 November 2013

Received in revised form 22 January 2014

Accepted 8 February 2014

Available online 11 March 2014

Keywords:

Alkane

Biomass

Single step

Deoxygenation

Isomerization

Zeolite

ABSTRACT

A single-step hydrotreatment of vegetable oil to produce high quality diesel-ranged alkanes over Ni/zeolite catalyst is devised. The Ni/zeolite catalysts prepared by incipient wetness impregnation method using SAPO-11, ZSM-5, ZSM-22, ZSM-23 and Beta zeolites as supports are evaluated in this single-step hydrotreatment process. The effects of the support and the metal loading amount are studied from the catalytic performance and characterization results obtained by techniques such as XRD, Physisorption, NH₃-TPD and Pyridine-IR. Over the 8 wt%Ni/SAPO-11 catalyst, 100% conversion of soybean oil is obtained at 370 °C, 4 MPa and 1 h⁻¹, with an organic liquid yield of 74.8% which is nearly 90% of the maximum theoretical liquid yield. In the organic products, the alkane selectivity is 100%, and more than 85% isomerization selectivity is achieved. In order to learn the detailed scheme of the single-step hydrotreatment process, the intermediates have been analyzed from which reaction pathways are proposed and discussed.

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1. Introduction

Effective conversion of renewable resource such as lipids to liquid fuels attracted growing interest [1–3]. The first generation biodiesel, that is, fatty acid methyl ester (FAME) produced by transesterification of the triglyceride, is one of the major fuel products derived from biomass and has been extensively studied [4–8]. However, high oxygen content, poor calorific value, high viscosity, as well as high pour point limit the FAME's direct application in vehicle engines. Diesel-range alkane produced by catalytic hydrotreatment of the lipids has been considered as one of the most promising energy derived from renewable resources [9–11]. This catalytic hydrotreatment process can be operated in existing refinery, and several related commercial applications such as Neste Oil's NExBTL, UOP and Eni's Ecofining, and Petrobras's H-BIO technologies have been operated on a large scale [12–14].

The existing commercial technologies generally consist of two steps, where the first step is the deoxygenation of lipids to

produce *n*-alkanes, while the second step is the isomerization of the *n*-alkanes to produce *iso*-alkanes with low freezing point and good flow property. In the last decade, conversion of higher aliphatic esters and their derivatives to *n*-alkanes by using heterogeneous catalysts had been extensively studied [15,16]. For example, the noble metal-based catalysts such Pd/C [17–19], Pt/C [20], Pt/Al₂O₃ [21], Pd/BaSO₄ [22,23] and Pd/SBA-15 [24] were utilized and studied in this process. Among them, the Pd/BaSO₄ exhibited the better performance, where a 99.5% conversion of methyl stearate and a 99.5% selectivity of linear decarboxylation products were obtained when hexane was used as a co-feed. Meanwhile, the processes by using non-noble metal-based catalysts had also been investigated [25–34], among which the hydrotreatment of microalgae oil over Ni/H-Beta [35] and Ni/ZrO₂ [36] reported recently attracted more attention for the high selectivity of the catalysts. The main products from the first step we have mentioned above are *n*-alkanes with a high pour point and high cloud point, which lead to a poor low-temperature performance, therefore, an isomerization process is often necessary.

Alkane isomerization is considered as one of the most important chemical process in the petroleum industry [37]. For example, the isomerization of short chain paraffin to produce gasoline with high octane value [38], the isomerization of long chain paraffin to produce lubricant with high viscosity index and the

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isomerization of C12–C24 alkanes to produce diesel with low freezing point [39]. Along with the development of these process, the bifunctional catalysts used in these process have been widely studied. These catalysts have both metal sites and acidic sites that work together as bifunctional catalysts to convert *n*-alkanes to iso-alkanes following the carbonium ion mechanism [40]. Since the lipid deoxygenation reaction is carried out on the metal active sites [41], these catalysts might also be active for lipids deoxygenation. Furthermore, as the main products produced by deoxygenation of lipids are *n*-alkanes, these catalysts can also convert the deoxygenation product to iso-alkanes.

However, combining the lipids deoxygenation and alkanes isomerization processes in a single step which is more economic and attractive was seldom reported [42,43]. In our previous work, a single-step hydrotreatment process combining deoxygenation and isomerization for producing high quality diesel-ranged alkanes over Pt/zeolite catalyst had been reported [44]. Over the 1 wt%Pt/SAPO-11 catalyst, 100% conversion of soybean oil, 100% alkane selectivity and more than 63% isomerization selectivity were obtained.

In this study, we report that the non-noble metal supported on zeolite can also efficiently catalyze the lipids conversion to high quality diesel-ranged alkanes in the single-step hydrotreatment process. The effect of the support, the effect of the metal loading amount and the influence of the reaction temperature were studied. Furthermore, in order to learn the detailed scheme of the single-step hydrotreatment process, the intermediates have been analyzed from which reaction pathways are proposed.

2. Experimental

2.1. Catalyst preparation

The SAPO-11, ZSM-22 and ZSM-23 zeolites were synthesized according to the methods of Flanigen et al. [45], Kokotailo et al. [46] and Rohrman et al. [47]. The Beta and ZSM-5 zeolites were purchased from Johnson Matthey Company. All of the reagents were of analytical grade and were used without further purification. We prepared the zeolite support following the preparation procedure for the industrial catalyst: the pure zeolite was blended with binder, that is, 30 wt% γ -Al₂O₃, and then the mixture was extruded, calcined at 550 °C for 4 h, and shaped before the metal component was loaded. The Ni/support catalysts used for the one-step hydrotreatment reaction were prepared by using the incipient wetness impregnation method with an aqueous solution of Ni(NO₃)₂. The 4 wt%Ni/SAPO-11, 8 wt%Ni/SAPO-11, 12 wt%Ni/SAPO-11, 8 wt%Ni/ZSM-22, 8 wt%Ni/ZSM-23, 8 wt%Ni/ZSM-5 and 8 wt%Ni/Beta catalysts were denoted as NS1, NS2, NS3, NZ2, NZ3, NZ5 and NB, respectively. All of the catalysts were reduced at 350 °C for 4 h under hydrogen atmosphere before the test.

2.2. Catalyst characterization

XRD measurements of the samples were performed by using a PANalytical X'Pert Pro X-ray diffractometer operated at 40 kV and 40 mA using nickel-filtered Cu K α radiation ($\lambda = 0.15404$ nm), covering 2θ between 5° and 55°. The surface area and pore volume of the samples were measured at –196 °C by using nitrogen adsorption according to the Brunauer–Emmett–Teller method (BET) by using a Micromeritics ASAP 2420 apparatus. The acidity of the samples was characterized by performing temperature-programmed desorption of ammonia (NH₃-TPD) with an automated catalyst characterization system (Autochem 2920, Micromeritics) with a TCD detector. We used a calibration curve to calculate the

ammonia amount by converting the peak area to concentration, and the number of weak, medium, and strong acidic sites was calculated by dividing the integrated peak area into ranges of 100–250, 250–450, and 450–600 °C, respectively [44]. Brønsted (B) and Lewis (L) acidic sites of the samples were determined by pyridine adsorption FTIR spectroscopy by using a Bruker Vertex70 IR spectrometer. Emeis' procedure was applied for the calculation here [48] [Eqs. (1) and (2)]:

$$C(\text{pyridine on B sites}) = 1.88IA(B) \times \frac{R^2}{W} \quad (1)$$

$$C(\text{pyridine on L sites}) = 1.42IA(L) \times \frac{R^2}{W} \quad (2)$$

where *C* is the concentration (mmol g^{–1} material); *IA*(B or L) represents integrated absorbance of Brønsted or Lewis band (cm^{–1}); *R* is the radius of catalyst disk (cm); and *W* is weight of disk (mg).

2.3. Single-step hydrotreatment reaction

The soybean oil used in this study was of food grade which had a composition of Palmitic: Stearic: Oleic: Linoleic: Linolenic = 10.2:3.7:22.8:53.7:8.6. The catalytic hydrotreatment of soybean oil was carried out in a three phase, fixed-bed reactor (10 mm i.d. and 600 mm in length). The reaction conditions were performed as follows: 300–380 °C of temperature, 4 MPa of hydrogen pressure, 300 mL.min^{–1} of hydrogen flow and 1–30 h^{–1} of liquid hourly space velocity (LHSV). In a typical run, 10 mL catalysts with the particle size of 20–40 mesh were loaded in the center of the reactor, while the empty space of the reactor was filled with inert silica with the particle size of 40–60 mesh. The reactor was then heated to 370 °C with a heating rate of 10 °C min^{–1}. After the temperature of the reactor was stable, the soybean oil was pumped into the reactor, and after reacting for 3 h, the products were collected and analyzed. The liquid yield (*Yield_L*%) was calculated as follows [Eq. (3)]:

$$Yield_L\% = \frac{(W_{\text{total}} - W_{\text{water}})}{W_{\text{feedstock}}} \times 100\% \quad (3)$$

where *W_{total}*, *W_{water}* and *W_{feedstock}* was the weight of the total products, the weight of water generated in the reaction and the weight of feedstock, respectively.

The liquid products were analyzed by using an Agilent 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a DB-5 capillary column (15 m × 0.32 mm × 1.0 μm). The Conversion *X* of soybean oil was calculated as [Eq. (4)]:

$$X = 100\% - C_{\text{(TG)}} \quad (4)$$

where *C_(TG)* is the sum of the concentrations of triglyceride determined by GC analysis (in %).

The selectivity *S_i* was calculated as [Eq. (5)]:

$$S_i = \frac{C_{(i)}}{X} \times 100\% \quad (5)$$

where *C_(i)* is the sum of the product concentration determined by GC analysis (in %).

The selectivity of decarbonylation plus decarboxylation, *S_{decarbonylation}* was calculated from liquid product analysis as [Eq. (6)]:

$$S_{\text{decarbonylation}} = \frac{C_{\text{(C17)}}}{[C_{\text{(C17)}} + C_{\text{(C18)}}]} \times 100\% \quad (6)$$

where *C_(C17)* and *C_(C18)* are the sum of the C17 alkanes and the sum of C18 alkanes concentration which are determined by GC analysis (in %).

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