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Catalytic conversion of stearic acid to fuel oil in a hydrogen donor

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ABSTRACT

Stearic acid (SA) was dispersed in tetralin (a hydrogen donor) and hydrotreated in a batch reactor over a fabricated sulfided NiMo/γ-Al_2O_3-β-zeolite catalyst to obtain a diesel-range fuel product. NiMo/γ-Al_2O_3-β-zeolite catalysts were prepared by loading the active components NiO and MoO_3 onto a mechanically mixed γ-Al_2O_3 and β-zeolite support, followed by a sulfurization procedure. The effects of the catalytic properties and reaction conditions on the hydrodeoxygenation of SA were investigated. The results showed that increasing the β-zeolite in the support leads to a decrease in SA conversion and an increase in the isomerization of products; increasing the NiO and MoO_3 mass fraction tends to promote the formation of alkene hydrocarbons and increase the level of isomerization; increasing the Ni molar fraction helps to promote both conversion and isomerization; and temperatures above 330 °C promoted the activities of the catalysts and tetralin. A nearly 90% SA conversion was achieved at 350 °C under H_2 at a pressure of 0.8 MPa for 2 h in tetralin. The total content of C16–C18 alkanes and alkenes in the products was about 98%, and the isomerized compounds accounted for 10–40 wt%.

Introduction

With the growing awareness of the global fossil energy demand and the growing concern about environment pollution, a lot of attention has been paid to the catalytic conversion of renewable fatty acid resources, e.g., conversion of vegetable oil or waste food oil to green and oxygen-free fuel oil [1–3]. The main conversion techniques include catalytic hydrogenation and catalytic cracking [4,5]. The most commonly used catalysts for hydrodeoxygenation (HDO) are sulfided supported metal catalysts (e.g., Co, Ni and Mo) with γ-Al_2O_3 or zeolite as a support [6–9] and noble metal catalysts (e.g. Pt and Pd) with an active carbon support [10–13]. Sulfided Ni, Mo, and NiMo-based catalysts have attracted much attention because of their low cost and high activity in the catalytic HDO of bio-oil with a high oxygen content [14–18]. It is generally considered that the activity of catalysts and fuel product distribution are significantly affected by acidic properties, metal active sites, the pore structures of catalysts, and process conditions [19–21]. Isomerization, an important catalytic activity, has been found to be an efficient way of improving fuel quality in petroleum refining such as lowing pour point, altering cetane number, and so on. So far, a lot of research has focused on clarifying the effect that the pore properties of catalysts and

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process conditions have on the conversion and selectivity of products; however, little research has been performed to investigate the effects of the acidic properties of catalysts and hydrogen-donating solvent on the catalytic hydrotreating process of fatty acids.

As a hydrogen donor, tetralin, which is widely used as solvent in the liquefaction of biomass and coal to produce liquid fuels, can disperse and stabilize intermediate products from the liquefaction process by offering active hydrogen under low H_2 conditions and consequently improves liquefaction efficiency and fuel quality [22–25]. Thus, the introduction of tetralin into the catalytic hydrotreating refining process of bio-oil is expected to provide a new insight into the understanding of the catalytic hydrotreating performance of a hydrogen-donating solvent and to further the development of a new hydrogen source as a substitute for high-pressured hydrogen, which is currently used in the chemical industry.

In this study, a series of supported catalysts with different acidic properties and active components were prepared by adjusting the γ-Al_2O_3/β-zeolite mass ratio in the composite support and the active metal oxide (NiO and MoO_3) content and Ni/Mo molar ratio in the catalysts. The present work is focused on the investigations of the catalytic activity and selectivity of sulfided NiMo/γ-Al_2O_3-β-zeolite catalysts and the hydrogen-donating activity of tetralin under different hydrotreating conditions and gives a greater understanding of the differences in HDO, isomerization, and other catalytic performances. This research could potentially provide a promising approach to develop an efficient HDO technique for transforming fatty acid resources into oxygen-free diesel-range fuels.

Materials and methods

Synthesis of the NiMo/γ-Al_2O_3-β-zeolite catalysts

γ-Al_2O_3 (A) and H-type β-zeolite (Si/Al = 25) (Z) were purchased from Nankai University Catalyst Co., Ltd. (Tianjin, China). Other reagents were of analytical grade and used as received. NiMo/γ-Al_2O_3-β-zeolite was prepared by impregnation method. The γ-Al_2O_3-β-zeolite (AZ) composite supports were firstly prepared by mechanically mixing γ-Al_2O_3 and β-zeolite with deionized water. The mixed suspension was evaporated at 80 °C to remove the water, dried in an oven at 105 °C for 1 h, and then calcined at 450 °C for 2 h. Afterward, $Ni(NO_3)_2$, $(NH_4)_2MoO_4$, and citric acid (CA) in their desired amounts were dissolved in deionized water to form a metallic salt solution. The obtained composite supports were slowly dispersed into the metallic salt solution. The mixture was then rotary evaporated at 50 °C to remove the water, and the obtained solid samples were dried, tableted, and calcined at 380 °C for 5 h. The catalyst samples were denoted *m*-y-NiMo/AZ-*x*, according to the different mass fractions of β-zeolite in the composite supports (*x*), the active component (NiO + MoO_3) mass fractions in the catalysts (*m*), and the Ni/(Mo + Ni) molar fractions (*y*). *x* was changed from 10% to 100%, *m* was changed from 10% to 30%, and y was changed from 10% to 35%.

Characterization of the catalysts

The obtained catalysts were characterized by X-Ray Diffraction (XRD, UItima IV, Rigaku, Japan) for the metal sites and by the temperature-programmed desorption of ammonia (NH_3-TPD) connected with a Residual Gas Analyzer (RGA200, Agilent) for the catalyst acid sites. The desorbed NH_3 was absorbed in 100 ml HCl (0.01 M), and NaOH solution (0.01 M) was used to titrate the NH_3-absorbed HCl solution. The total acidity was calculated from the amount of HCl and NaOH consumed. The distribution of the weak acid, medium acid, and strong acid was calculated from the peak area from Gaussian Fitting of the NH_3-TPD profiles, acquired from RGA200.

N_2 adsorption–desorption isotherms were measured using a Quantachrome instrument (Autosorb-IQ-C, Florida, USA) over samples evacuated at 250 °C for 6 h at least. The specific surface area (S_{BET}) was determined by the Brunauer–Emmette–Teller (BET) method. The total pore volume (V_{Total}) was calculated from the volume of N_2 adsorbed at the relative pressure P/P0 of 0.994. The volumes of the mesopores (V_{Meso}) and micropores (V_{Micro}) were calculated from the desorption branch of the adsorption–desorption isotherms by the Barrett–Joyner–Halenda (BJH) method and Horvath–Kawazoe (HK) method, respectively. The average pore radius was obtained from the adsorption–desorption experiment.

Catalytic hydrodeoxygenation of stearic acid

Catalytic experiments were carried out in a 20 ml batch-type reactor, which was fixed on a shaker and shaken at a constant speed. 0.1 g of the catalysts was sulfided in situ prior to the HDO experiments by means of dimethyl disulfide (DMDS) under H_2 at 5 MPa pressure and 320 °C for 3 h. After sulfurization, the reactor was cooled to about 100 °C, and the remaining DMDS, residual gases, and vapor were then released. Immediately, 1.2 g of stearic acid (SA) and 4.8 g of tetralin were added into the reactor and reacted under various conditions: temperature (300–350 °C), H_2 pressure (0.8–5 MPa), and time (1–3 h).

Product analysis

The liquid products were firstly methyl esterified according to the standard methods of GB/T 17376-2008. The components in the products were qualitatively analyzed by GC–MS (GC 7820A, MS 5977E, Agilent) and quantitatively determined by GC-FID (9792II, Fuli, China). The GC–MS conditions were as follows: a column of HP-5MS (50 m × 0.25 mm × 0.25 μm) was used; the carrier gas (He) velocity was kept at 1.2 ml/min. The oven program was set as follows: 5 min isothermal at 60 °C, heated to 300 °C at 10 °C/min, and then the temperature was held constant for 15 min; the injector and interface temperature were maintained at 290 °C and 300 °C, respectively. The GC-FID conditions were as follows: a column of HP-5MS (30 m × 0.2 mm × 0.3 μm) and the same column oven temperature program as used in GC–MS analysis were used.

The SA conversion and the level of isomerization of the products were used to evaluate the efficiency of the catalytic

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