



Catalytic hydroprocessing of fatty acid methyl esters to renewable alkane fuels over Ni/HZSM-5 catalyst



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ARTICLE INFO

Article history:

Received 26 November 2014
 Received in revised form 2 August 2015
 Accepted 11 August 2015
 Available online 12 September 2015

Keywords:

Hydroprocessing
 FAMES
 Alkane fuels
 Ni/HZSM-5

ABSTRACT

A series of Ni/HZSM-5 catalysts with different Ni loading and Si/Al ratios were prepared by incipient wetness impregnation. The physicochemical properties of the catalysts were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂-adsorption, temperature-programmed desorption of ammonia (NH₃-TPD), and thermogravimetric (TG) analysis. Moreover, their catalytic performance was investigated for the hydroprocessing of long-chain unsaturated fatty acid methyl esters (FAMES) to renewable alkane fuels using a high-pressure fixed bed reactor system with a facility for online analysis. The different Ni loading and Si/Al ratios of the catalysts, as well as the influence of reaction conditions such as temperature, pressure, H₂/oil molar ratio, and liquid hourly space velocity (LHSV), were studied in detail. The NiO aggregates dispersed on the surface of the support clearly increased the acidity after H₂ reduction, thus significantly affecting the catalytic performance. Temperature and pressure played crucial roles in the conversion of FAMES and selectivity for gasoline or jet or diesel alkane. Hydroprocessing over 10 wt% Ni/HZSM-5 (Si/Al = 25) at 280 °C, a H₂ pressure of 0.8 MPa, an LHSV of 4 h⁻¹, and with a highly purified H₂/oil molar ratio of 15 led to a high selectivity of 88.2% for C₅–C₁₈ liquid alkanes, which includes 8% of gasoline alkane, 32.5% of jet alkane and 47.7% of diesel alkane, along with appropriate isomerization selectivity of 27.0%, while the conversion of FAME reached 85.1%. To demonstrate the potential of this catalyst for practical applications, its stability in the hydroprocessing of FAMES was also investigated. The conversion of FAMES decreased to 30.1% over 10 wt% Ni/HZSM-5 (Si/Al = 25) after operation for 80 h. Catalyst deactivation was predominantly caused by the deposition of carbon which causes blockage of the pores for FAMES as evidence from TG analysis.

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1. Introduction

Owing to the economic expansion worldwide, energy consumption is rapidly increasing. Moreover, global demands for renewable alkane fuels and regulations to reduce the industry's environmental footprint are also increasing. Biodiesel, which is composed of various fatty acid methyl esters (FAMES), is a type of renewable and clean fuel; it satisfies the industrial requirement for an alternative carbon reduction strategy wherein no modifications to aircraft or engine are required [1,2]. However, the energy density and oxidation stability of FAMES are significantly poorer than those of fossil

diesel, which is caused by the presence of an excess of oxygen in them [3,4].

In recent years, the diesel and jet fuel range alkanes produced by the heterogeneous catalytic hydrotreatment of the FAMES derived from biomass oils such as plant oils, animal fats, and waste cooking oils have received increasing attention. Typically, these biomass oils contain C₁₄ to C₂₄ fatty acids, with a predominance of C₁₈ fatty acids; because these fatty acids have fuel properties similar to those of their petroleum counterpart, they are adequate for the production of hydrocarbons in the diesel range. Recently, oil refineries in many countries have been utilizing the hydroprocessing of FAMES to obtain an oxygenate-free fuel and to decrease their dependence on petroleum as well as for environmental reasons [4,5]. Synthetic jet fuel can also be produced by the hydroprocessing of FAMES, followed by the essential degradation of C–C bonds (hydrocracking). Therefore, aviation leaders have turned to mechanical and technological enhancements for reducing fuel burn and

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greenhouse gas emissions. According to statistics, the hydroprocessing of biomass feedstock provides for a reduced environmental footprint—approximately 30% reduction for a sustainable cultivated feedstock, when blended 50/50 with the conventional jet fuel [6].

The hydrodeoxygenation (HDO) of different model long-chain esters and acids over different catalysts has been previously reported [7–10]. Another catalyst-based approach toward the conversion of vegetable oils is catalytic cracking at low pressures, especially over zeolites, such as HZSM-5, Hbeta, and USY, as well as mesoporous materials such as Al-SBA-15 [10–14], facilitated by their crystalline porous structure, high cracking activity, and good thermal or hydrothermal stability.

Further, hydroprocessing is affected not only by the catalyst but also by the operating conditions. Yang et al. [15] investigated process parameters such as temperature, weight hourly space velocity (WHSV), pressure, and H₂/oil ratio for the hydrotreatment of C₁₈ fatty acids over sulphided NiW/SiO₂-Al₂O₃. They found that the above mentioned parameters significantly affected the performance of the catalyst. Bezerigianni et al. [16–18] have focused on the hydroprocessing of waste cooking oil and found that lower temperature, pressure, and H₂/oil ratio as well as a higher liquid hourly space velocity (LHSV) promote the formation of diesel alkanes.

The process of producing renewable alkane fuels is based on a traditional refining hydroprocessing technology. It includes a two-step process: (1) adding hydrogen to remove oxygen from the feedstock (there are three reaction pathways to remove oxygen, as shown in Scheme 1, and (2) further refining the product thus obtained to meet the required specifications (for example, low-temperature fluidity), such as hydroisomerization and hydrocracking [19]. In light of this, many catalysts have been chosen to catalyze the process: traditional supports such as γ -Al₂O₃ [20–22] or non-acidic catalysts [22,23] mainly produce normal paraffins as alkane products with poor low-temperature properties; noble-metal-based catalysts incur high cost, thereby limiting their large-scale application [24,25]; Co- and Mo- metal-based sulfided catalysts often exhibit high hydroprocessing conversion but sulfur leaching could contaminate the alkane products [23,26]. However, HZSM-5 has been proven to exhibit suitable Brunauer–Emmett–Teller (BET) surface area and acidic centers for catalytic hydroprocessing [27,28]. Meanwhile, the use of zeolite catalysts for the one-step hydroprocessing of FAMES to normal and iso-alkanes needed a deeper study.

This study aims to selectively produce C₅–C₁₈ renewable alkanes (gasoline or jet or diesel alkanes) by the catalytic hydroprocessing of long-chain unsaturated FAMES using a Ni-modified HZSM-5 catalyst (Si/Al = 25) and to investigate the influence of process parameters (temperature, pressure, H₂/oil molar ratio, LHSV). Moreover, the selectivity toward deoxygenation and decarboxylation or decarbonylation (which determine the relative amounts of C₁₈ and C₁₇ normal and iso-alkanes) is reported. The stability and deactivation of the catalyst are also investigated.

2. Material and methods

2.1. Materials

Long-chain unsaturated FAMES produced by the transesterification of triglycerides were provided by Tianjin Guangfu Fine Chemical Industry Institute, China. Table 1 shows the fatty acid compositions of FAMES.

All chemical reagents were obtained from commercial suppliers: nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O] (98%, Reagent Plus) from Tianjin Fuchen Chemical Factory; n-nonadecane analytical standard ($\geq 99\%$, GC assay) was obtained from Aladdin Chinese

Table 1
Fatty acid compositions^a of FAMES.

FAMES	Fatty acid compositions ^a of FAMES structure	Formula	Compositions (wt%)
Methyl oleate	C _{18:1} ^b	C ₁₉ H ₃₆ O ₂	99.0
Methyl octadecanoate	C _{18:0}	C ₁₉ H ₃₈ O ₂	0.8
Methyl linoleate	C _{18:2}	C ₁₉ H ₃₄ O ₂	0.2

^a Fatty acid composition was assigned on the basis of the alkyl chain length.

^b The ratio represents the number of carbon atoms to number of C=C double bonds.

Reagent Co., Ltd. The support for HZSM-5 (Si/Al = 25, 50, 150, 360) zeolites was purchased from Nankai University, China.

2.2. Catalyst preparation and characterization

The Ni/zeolite catalysts with different Si/Al ratios were prepared by the impregnation of the HZSM-5 zeolite carriers in an aqueous solution of Ni(NO₃)₂·6H₂O, which was used as the metal precursor. The resultant suspension was stirred for 6 h at ambient temperature, further dried at 110 °C for 12 h, followed by calcination at a rate of 10 °C/min from ambient temperature to 550 °C, maintained for 5 h.

X-ray diffraction (XRD) measurements of zeolite samples with different Si/Al ratios were conducted on a Phillips X'Pert MPD (PW3040/60) diffractometer operating at 40 kV and 40 mA using Ni-filtered Cu-K α radiation. The sample was measured using a scan rate of 1°/min over the range of 2 θ = 5–80°. The metal particle size was calculated using the Scherrer equation (1) on the basis of the diffraction peak width.

$$d = \frac{K\lambda}{\beta} \cos \theta \quad (1)$$

In addition, the morphology and size of the zeolite were investigated by scanning electron microscopy (SEM; Hitachi S-4800 FESEM) operating at 2.0 kV. Transmission electron microscopy (TEM) images of the catalyst were recorded on a JEM-2100HR system operating at 100–200 kV.

The Si/Al ratio with different HZSM-5 zeolite catalysts was measured by X-ray fluorescence (XRF) using a PANalytical B.V. analyzer.

Nitrogen adsorption–desorption experiments were conducted to obtain specific surface areas by BET and pore size distribution of the sample using an American Quantachrome ASI/QM002-2 automated system at –196 °C. The sample was activated at 300 °C for 6 h under vacuum prior to measurements. The Horvath–Kawazoe (HK) method was adopted to determine the pore size distribution of the catalysts.

The temperature-programmed desorption of ammonia (NH₃-TPD) was tested using an ASI/QACIV200-2 multifunctional chemical adsorption instrument. The sample (0.15 g) was initially activated under a He flow at 500 °C for 30 min at a ramp rate of 40 °C/min. Ammonia was adsorbed to saturation after cooling the system to 100 °C for 1 h. Subsequently, after removing excess ammonia under a He flow for 1 h, the sample was heated to 750 °C at a ramp rate of 10 °C/min to desorb ammonia. For the quantification of the amount of acidic sites, a standard HZSM-5 zeolite (Si/Al = 25) with a known acid site concentration was used to calibrate the signal.

The TG analysis of the spent catalyst was conducted at an air flow rate of 30 mL/min by increasing the temperature from 40 °C to 850 °C at 10 °C/min.

2.3. Hydroprocessing

Fig. 1 depicts the hydroprocessing of FAMES in a high-pressure fixed bed reactor. First, 0.8 g of the catalyst (40–60 mesh) was

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